DEVELOPMENT OF SELF-DESTRUCTING FILTER CAKE

A Thesis

by

AMENEH ROSTAMI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2010

Major Subject: Petroleum Engineering

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ABSTRACT

Development of Self-destructing Filter Cake. (August 2010)

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The main goal of drilling a horizontal well is to enhance productivity or injectory by placing a long distance drain-hole within the pay-zone. Poor drilling fluid design results in difficulties such as poor hole cleaning, excessive torque or drag, wellbore instability, stuck drill string, loss of circulation, subsurface pressure control, poor cement jobs, and difficulties associated with running electric logs and formation damage can result. Neither of the conventional chemical cleaning methods can overcome problems for filter-cake removal in long horizontal and maximum reservoir contact wells because of limitations such as the complex geometry of wells, non-uniform chemical distribution, low contact between cleaning fluids/filter cake, and high chemical reaction rate, especially at high temperatures.

This study describes a novel self-destructing drilling fluid system. Filter cakes are formed from a formula of drilling fluid that have a mixture of solid acid precursor and particulate solid acid-reactive materials. Then in the presence of water, the solid acid precursor (polylactic acid) hydrolyzes and dissolves, generating acids that then dissolve the solid acid-reactive materials (calcite). It effectively stimulates the horizontal section

right after drilling and eliminates acidizing, resulting in significant cost savings, and improves filter-cake removal, thus enhancing the performance of the treated wells.

A series of experiments have been run in the lab to determine the efficiency of this new system. Properties of this drilling fluid are measured. Experiments on solid acid particle size showed that the best size-distribution of solid acid precursor and solid reactive material to make a self-destructing filter cake is fine particles of calcium carbonate used as weighting material with 150 microns polylactic acid as solid acid precursor. By comparison of the results of the experiments at different temperatures, 230º F has been chosen as the best temperature for running experiments. The self-destructing drilling fluid systems need enough time for the solid acid to be hydrolyzed and therefore remove the filter cake. After 20 hours of contact with the water as the only cleaning solution, about 80% of the filter cake was removed. Calcite is found to be the dominant compound in the sample of remained filter cake, which was proved by x-ray diffraction tests. Secondary electron microscopy (SEM) results show the morphology of the remained filter cake sample and confirm the crystalline area of calcite.

DEDICATION

Dedicated to my mom, dad, sister and brother and most importantly my dear husband

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NOMENCLATURE

C	Conversion Constant
CMC	Carboxy-methyl Cellulose
DIF	Drill-in Fluid
EOR	Enhanced Oil Recovery
H_p	Hydrostatic Pressure (psi)
LCM	Lost Circulation Material
MD	Mud Density (lb_m/gal)
OBM	Oil-based Mud
PV	Plastic Viscosity (cp)
SBM	Synthetic-based Mud
T	Temperature (deg F)
TVD	True Vertical Depth (feet)
WBM	Water-based Mud
YP	Yield Point (Ib_f/100 ft^2)

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INTRODUCTION

Introduction

Overbalanced drilling of wells in petroleum reservoirs is a process that causes a cross-flow filtration, which leads to a filter cake buildup over the face of the porous rock and filtrate invasion into the reservoir. Drilling fluids are formulated to protect producing intervals by:

- Mechanically sealing exposed pore space openings in boreholes by forming thin, tough and impermeable filter cakes
- Stabilizing the wellbore during completion by strengthening the wellbore
- Allowing easy cleanup after drilling and completion

Proper filter cake formation, formation protection, and maximizing return permeability are the factors that could determine the best design of the drilling fluid. Most drill-in fluids contain weighting solids. The pressure overbalance required between the drill-in fluid and reservoir pressure to keep the well under control will force the weighting solids to enter the formation and cause damage.

Horizontal wells are more susceptible to formation damage than their vertical counterparts for the following reasons (Mohammed 2001):

- Drilling fluids are in longer contact with the formation. In a vertical well, drilling mud may only be in contact with pay zone a matter of hours, while in a horizontal wells the time may be measured in weeks

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This thesis follows the style and format of *SPE Production & Operations*.

- Most horizontal wells are completed open hole and they are not cased and perforated. Relatively shallow damage, which can be easily perforated on standard vertical wells, remains a major source of permeability reduction in many horizontal wells
- Because of the length of the well in the pay zone in horizontal wells, high drawdown is difficult to obtain in these wells. This makes it much more difficult to clean up damage because of invaded fluid or solids
- Stimulation of horizontal wells is extremely difficult and expensive. Thus once formation damage occurs, it is usually permanent in nature

Demand for horizontal wells has increased recently because of advantages like maximizing reservoir exposure, targeting multiple reservoirs from a single platform, reducing drawdown to minimize water and gas conning problems, and exploiting thin pay zones to increase reservoir drainage and productivity. Very often for horizontal wells, water-based polymer type mud systems are used as drilling fluids. Because of the nature of the polymers, the filter cakes formed by these types of fluids are tough and not easily degradable. Introduction of both mud solids and polymers into the formation, changed values of fluids saturation in the pore spaces, and the reaction between the filtrate and the pore contents and/or the matrix materials result in a reduction of the formation's original permeability.

Removing the filter cake can be accomplished by mechanical means (scraping, jetting) or by subsequent addition of a fluid that has some chemical as removing agent such as an acid or an enzyme to dissolve at least a portion of the filter cake (Willberg

and Dismuke 2009). Another method can be by manipulation of the physical state of the filter cake, such as using emulsion inversion techniques (Todd et al. 2004).

Some chemical cleanup solutions for $CaCO_3$ based drill-in filter cake could be acids (Siddiqui and Nasr-El-Din, 2005; Al-Yami and Nasr-El-Din, 2009), chelating agents (Burton et al. 2000), oxidizers (Almond, 1982; O'Driscoll et al., 1998), enzymes (Hanssen et al. 1999), emulsions (Al-Riyamy 2000), micro emulsions (Quintero et al. 2005), solid-free brines (Al-Yami and Nasr-El-Din 2009), in situ generated acids (Al Moajil and Nasr-El-Din, 2007; Binmoqbil et al., 2009; Alotaibi et al., 2007) or a combination of these materials.

Oxidizers and acid breakers have been used for many years to remove the filter cake produced by polymer-based drilling fluids. Although these materials could be reasonably effective in attacking individual components of the cake, they are not necessarily efficient when confronted with the tight composite cake laid down on the formation. Therefore, in many cases unreacted polymers stay in place and degrade partially (Stanley et al. 1999).

Another common disadvantage of these treatments is that they are highly reactive and may remove the filter cake at the point of circulation before the treatment can be placed over the openhole interval (Todd et al. 2004). Strong acids can increase the permeability of many formations by dissolving rock minerals, but at the same time can cause additional permeability damage if dissolved components reprecipitate (Siddiqui and Nasr-El-Din 2005). Consequently, a need exists for cleanup solutions that have a

delayed effect on filter-cake integrity, allowing the cleanup solution to be circulated across the entire interval.

Thus to achieve an effective method to remove and complete a well, we need to develop a fluid that has the functions of both drilling and completion fluids and can reach the total depth of maximum reservoir contact (MRC) wells. This can result in a significant cost savings by elimination of acidizing using coiled tubing or any other means. Therefore, filter cake removing efficiency and performance of the treated wells improves.

In this study, a method and composition will introduce for the drilling fluid as a self-destructive composition to form filter cake in wellbore and subterranean formations. This fluid loss additive and filter cake will form from a formula of drilling fluid that has a mixture of solid acid precursor and particulate solid acid reactive material. This fluid will create a chemically meta-stable filter cake that prevents fluid leakoff and formation damage during the drilling process but readily cleans up over time. As the solid acid precursor hydrolyzes, it will form an acid that attacks the carbonate or other particles. Since the solid acid precursor and carbonates or other materials are intermingled during deposition, the cleanup process is uniform and extensive.

This treatment could be used in various oilfield treatments such as drilling, completion and stimulation. By using this new and novel technology, it is no longer necessary to use mechanical and chemical means for removing filter cake or inject any additional fluid (Willberg and Dismuke 2009).

Pore size distribution of the rock onto which the filter cake is to be deposited, determines the particle size of individual components of the mixture as they relate to use as a fluid loss additives and as filter cake components. For the method described here, particle size distribution may be selected as a compromise between those that are optimal for fluid loss control or filter cake formation and those that are optimal for self-destruction at desired time and rate. Polylactic acid is chosen to function as solid acid precursor and calcium carbonate is used as solid-acid reactive material (weighting material). The most important factors that should be considered for choosing a solid acid precursor are that it must:

- Generate acid at a desired rate (after a suitable delay if needed)
- Be compatible with and not interfere with the function of other components of the fluid

An acid-reactive material is selected that dissolves in the evolving fluid at a suitable rate and is compatible with the function of other components of the fluid (Willberg and Dismuke 2009). A particular advantage of these materials is that the solid acid precursors and generated acids are nontoxic and biodegradable. The solid acid precursors are often used as self-dissolving structures. Calcite is known to be an excellent fluidloss additive. It has some good properties that are useful for this new technique. For example, calcite is not soluble in water, even at 150 °C.

Once this research is completed, self-destructing drilling fluids will be used to drill long horizontal and MRC wells, resulting in higher productivity. These fluids will

have the ability to effectively stimulate the whole horizontal reservoir and MRC wells immediately after drilling. No technology is available today that can do this.

DRILLING FLUIDS

Drilling Fluid Technology

Drilling fluids are primarily used to cool, clean and lubricate the bit and to continuously remove the cutting from the borehole. By progressing drilling fluid technology, they became more sophisticated and turned to complicated mixture of liquids, solids and chemicals. Many additives were introduced for any conceivable purpose. The fluid characteristics affect cores, wire line logs and drill return logs. The drilling fluid must permit the securing of all information necessary for evaluating the productive possibilities of the formations penetrated. Drilling fluids can be studied from two standpoints: technology and chemistry. These two standpoints will be discussed here.

Variety of downhole conditions result in the choice of different types of mud. When choosing a particular mud, factors such as the depth, type of formation, and local structure etc. should be considered (Oil Field Familiarization Training Guide May 1996). Drilling mud must have some functions and corresponding properties such as to:

- Control subsurface pressures and prevent caving (mud density)
- Remove cuttings from the borehole (viscosity)
- Suspend cuttings when circulation stops (gel strength)
- Cool and lubricate the bit and drillstring (additive content)
- Wall the borehole with an impermeable filter cake (fluid loss)
- Release the cuttings at the surface (viscosity/gel strength)
- Help support the weight of the drill-string/casing (density)

- Ensure maximum information from the formation
- Do all of the above, without damage to the circulation system

Controlling Subsurface Pressures

To prevent the formation fluids from flowing into the borehole, the pressure must be adequate at all times. The pressure of the mud column is a function of mud density and column height. The formation fluids can enter the well if the density of the mud falls below that which is needed to hold back formation pressure. This is termed “kick”.

There may be a severe reduction in mud density resulting in uncontrolled flow if this condition is allowed to continue unchecked for even a short period of time. This is termed “blowout”.

On the other hand, having a mud that is weighted too high is neither practical nor economical. It causes low rates of penetration and also fracturing weak formations. It may cause loss of drilling mud into the formation which causes a high lost in circulation (Oil Field Familiarization Training Guide May 1996).

Density is an important factor in preventing unconsolidated formations from caving into the borehole.

Effect of Mud Weight on Drill Returns Logging

Hydrostatic Pressure is the pressure which exists due to the drilling fluid weight and vertical depth of the column of fluid.

$$H_p = C \times MD \times TVD \quad \text{.....} \quad (2.1)$$

where:

C = Conversion constant

MD = Mud Density

TVD = True Vertical Depth

If:

Hp = psi	Hp = bars
MD = lbm/gal or ppg	MD = g/cc
TVD = feet	TVD = meters
C = 0.0519	C = 0.0981

If hydrostatic pressure exceeds formation pressure it causes the formation fluids to be flushed back into the formation being penetrated, either at the bit or just ahead of it. This may happen at any time, whether marginally or greatly overbalanced. Under this condition circulation is lost. Furthermore, cuttings, drilling mud and any formation fluids they may contain are also lost.

The lost circulation behavior in any zone generally indicates the type of porosity of the formation into which the fluid is being lost. Examples are:

a) Coarse, permeable unconsolidated formations

Before an impermeable filter cake is formed in these types of formations, there is normally some loss by filtration into them. In the case of small pore openings, regular seepage loss and partial returns are maintained. But in formations with large pore openings, all the mud may be lost.

b) Cavernous and vugular formations

In these formations, loss is usually sudden and finite amount, after which full returns are maintained.

c) Fissured or fractured formations

Natural fractures or induced fractures that may be opened by hydrostatic pressure cause large and continuous losses of drilling mud in these types of formation.

If hydrostatic pressure is approximately equal to or less than the formation pressure, it may allow entry of formation fluids, depending on permeability. In low permeability formations (shale), caving may occur, making cuttings analysis difficult (Oil Field Familiarization Training Guide May 1996).

Removing and Suspending the Cuttings

One of the main functions of drilling fluid is to have the ability to carry the cuttings up the borehole and suspend them when circulation is stopped. The speed at which the mud travels up the borehole (annular velocity), and the viscosity and gel strength of the drilling mud are the most important factors involved.

Viscosity

In drilling fluid terminology, the resistance that the drilling fluid offers to flow when pumped is regarded as viscosity. The amount and character of the suspended solids determine the viscosity of the drilling fluid. The viscosity affects the ability of the drilling fluid to lift the rock cuttings out of the borehole. This property is measured in the field by using a "Marsh Funnel". The funnel is filled with one quart of drilling fluid, and the elapsed time to empty the funnel is recorded in seconds. The measurement of "funnel viscosity" is "sec/qt" (seconds per quart). This value can range from 20 to 80, but is normally maintained between 40 and 50.

Gel Strength

Gel strength refers to the ability of the drilling fluid to develop into a gel as soon as it stops moving. Its purpose is to suspend the cuttings and mud solids (weight material), while they are in the borehole and not permit cuttings to settle around the bit when circulation is halted. In general, gel strength should be low enough to:

- Allow the cuttings to be removed at the surface
- Permit entrained gas to be removed at the surface
- Minimize swabbing when the pipe is pulled from the borehole
- Permit starting of circulation without high pump pressures

The gel strength is most commonly determined with a "Fann VG (Viscosity/Gel) Meter" and is expressed in $lb_f/100ft^2$ (pounds per 100 square feet). Drilling muds ordinarily have gel strengths between 5 and 30 $lbs/100ft^2$.

Effect of Viscosity and Gel Strength on Drill Returns Logging

If the viscosity or gel strength (or both) is too high, the drilling fluid tends to retain any entrained gas as it passes through the surface mud cleaning equipment, with the effect that the gas may be recycled several times. Swabbing of the borehole may also introduce extraneous gas anomalies.

Fine cuttings may be held in suspension so they cannot be removed at the shale shakers and settling pits, thus recycling and contaminating the cuttings samples. Also, cuttings consisting of clays or other dispersible material may be dissolved (Oil Field Familiarization Training Guide May 1996).

Cooling and Lubricating the Bit and Drill String

Practically any fluid that can be circulated through the drillstring will serve to cool the bit and drillstring. Lubrication, however, commonly requires special mud characteristics that are gained by adding oil, chemicals and other materials.

Walling the Borehole with an Impermeable Filter Cake

The hydrostatic pressure of the column of drilling fluid exerted against the walls of the borehole helps prevent the caving of unconsolidated formations. A plastering effect, or the ability to line permeable portions of the borehole with a thin, tough filter cake, is also produced.

Control of the filtration rate (water loss) is necessary for two reasons:

1. A poor quality filter cake may cause excessive water loss and produce an excessively thick filter cake, thereby reducing the diameter of the borehole which increases possibility of sticking the drillstring and the swabbing effect when pulling the drill pipe.

2. High water loss can cause deep invasion of the formations, making it difficult to interpret wire line logs (Oil Field Familiarization Training Guide May 1996).

Drilling Fluid Chemistry

The list of chemical additives used to develop functions of the drilling fluids described above is extensive, but we can categorize them into three basic drilling fluid types:

- Water/clay muds
- Oil/water clay muds

• Compressed gases

Water/Clay Muds

A common type of drilling mud is water/clay mud that consists of a base liquid phase of water. The clay materials could be reactive or non-reactive solids that are suspended in the water and are added to the mud to give it special properties. The three main components of every water-based mud system are water and reactive and inert solids.

Water

We may use fresh water or salt water as a base phase in water-based muds. In offshore drilling seawater is commonly used. In sensitive formations such as for drilling thick evaporite sequences we add salts to water to prevent them from dissolving and causing washouts. Saturated saltwater is also used for shale inhibition.

Reactive Solids

Clays

Clays are a basic component of these muds and are solids that affect the viscosity, gel strength and water loss of the drilling fluid and are commonly referred as gel.

Common clays are:

• Bentonite - for fresh water muds

• Attapulgite - for saltwater muds

• Natural formation clays which hydrate and enter the mud system

Dispersants

Examples of dispersants are tannins, quebracho, phosphates, lignite and lignosulphonates. These components reduce the attraction between particles and therefore reduce the viscosity by adsorption onto clay particles.

Filtration Control Agents

These components develop a firm impermeable filter cake on the formation and control the amount of water loss into permeable formations, due to the pressure differential.

Example of filtration loss agents are:

• Starch – pre-gelatinized to prevent fermentation

• Sodium carboxy-methyl cellulose (CMC) - organic colloid, long chain molecules which can be polymerized into different lengths or "grades". The grades depend on the desired viscosity.

• Polymers - for example cypan, drispac, used under special conditions

Detergents, Emulsifiers and Lubricants

These chemicals are used for lubrication and assist the cooling functions of the drilling fluid. Also used for a spotting fluid in order to free stuck pipe.

Defoamers

These materials prevent mud foaming at the surface in treatment equipment.

Sodium Compounds

Precipitate or suppress calcium or magnesium which decreases the yield of the clays.

Calcium Compounds

Inhibit formation clays and prevent them from hydrating or swelling.

Inert Solids

Weight Material

Weighting materials are used to control mud density. They are high-density finely ground materials. Common weight materials are barite, hematite and calcium carbonate.

Lost Circulation Material (LCM)

These materials are used to plug the point of loss and bridge the formation. These materials have different particle sizes and come in different types. Some examples of these materials are as follows:

- Fibrous: wood fiber, leather fiber
- Granular: walnut shells (nut plug), fine, medium, coarse
- Flakes: cellophane, mica (fine, coarse)
- Reinforcing Plugs: bentonite with diesel oil, time setting clays, attapulgite and granular (squeeze)

Sometimes these materials don't have enough functionality and it is necessary to cement the formation.

Antifriction Material

This is added to the mud system to reduce torque and decrease the possibility of differential sticking. The most frequently used material is inert polyurethane spheres.

More frequently it is used on high angle directional wells, where torque and differential sticking are a problem.

Oil/Water/Clay Muds

These types of drilling fluids have both oil and water inside the mud formula. Two basic types of oil/water mud systems are:

1. Emulsion (oil/water) System

In this type of mud the base phase is water and then diesel or crude oil is dispersed in a continuous phase of water.

2. Invert Emulsion (water/oil) System

In this type of drilling fluid, the continuous phase is diesel/crude oil and the water is dispersed in this base phase.

These mud systems have very significant advantages that make them very special completion fluids for drilling production wells. Despite the high cost, difficulty of running, and the complexity of geological evaluation, they are non-reactive with clays and their filtrate will not damage the formations. They are used also in certain troublesome evaporite and clay sections. Apart from these emulsions containing roughly equal portions of oil and water, there are true oil-based muds which may contain only 5 percent water. When oil-based mud systems are in use, special considerations must be made regarding formation evaluation (Oil Field Familiarization Training Guide May 1996).

Compressed Gases

These mud systems are applicable only in areas where there is little formation water. The compressed air or gas is circulated the same as conventional drilling mud, except compressors are used instead of mud pumps. In the case of using compressed air or natural gas a foaming agent should be used to improve carrying capacity(Oil Field Familiarization Training Guide May 1996)

Selecting a Drilling Fluid

The success of a drilling operation strongly depends on the selection of the drilling fluid. Factors such as different base liquids (water or oil), different dominating cations in the aqueous phase, different chemical additives, and also diverse physical properties make drilling fluids with different behavior. But no fluid is suitable for all situations.

The name of the drilling fluid could be as long as necessary for the desired degree of precision (e.g., sea water lignosulfonate mud, saturated salt mud, potassium mud, relaxed-fluid loss oil mud, gypsum mud and polymer mud).

Numerous factors should be considered in drilling fluid selection. The most important are safety, evaporate zones, high temperatures and pressures, environment loss zones, shale problems, well trajectory and economics. Taking these one at a time, and in order, will in most cases lead to a proper choice of drilling fluid (Bleier 1990).

Safety Issues (Well Control, Gas Hydrates, H_2S)

Safety is very important while drilling. To control the well, drilling fluid should be able to carry the mud weight. In a kick situation the speed and ease with which a mud

can accept weighting material is very important. Although most mud types are satisfactory in this respect, at mud weights above 15 lbm/gal, in muds that contain polymers, some dispersant should be added. For oil muds, the oil/water ratio should be higher than 50/50.

Gas hydrate is a problem in deep water drilling and can make some mechanical difficulties in well control operations. Adding salt to the drilling fluid is a solution in deepwater drilling because a high salinity mud tends to suppress hydrate formation. Mud composition also has some effect on preventing hydrates.

The best and safest drilling fluid for H_2S situation is a mud that contains 10 lbm/bbl excess lime plus a sulfide scavenger. Lime and oil muds are the only two mud types that are truly compatible with this requirement (Bleier 1990).

Evaporite Zones

In massive evaporate zones, the drilling fluid must be presaturated with evaporite. Otherwise the evaporate zone tends to leach out excessively into the water-based drilling fluid.

Gypsum muds are a natural choice for massive anhydrite sections. A saturated salt mud or an oil mud is required in thick salt sections. A properly formulated oil mud is a good choice for any evaporate zone.

High Temperature and Pressures

For most water-based mud types at downhole temperatures of 250-350^{o}F, some problems like high temperature gelation and fluid loss may occur. At elevated temperatures and pressures oil muds are viable and less costly and could be used as an

alternative for water-based muds. Some water-based muds are specially formulated and can be stable at 400° to 450 °F at mud weights up to 18 lbm/gal (Bleier 1990).

Environmental Considerations

Environmental considerations depend on the well location. They are many and various and can limit the choice of mud type. In some areas using oil-based muds is prevented. In others salt muds are avoided and chromium treated muds are prohibited in some other areas. The toxicity of special additives can be tested by drilling-fluid bioassay tests. Finding adequate replacements for environmentally objectionable systems is the highest priority in drilling fluids (Bleier 1990).

Severe Loss Zones

Lost circulation solids are added to the drilling fluid to seal that part of the formation where loss of the mud occurs, called thief zones. We may be able to anticipate the fluid loss in these zones in advance. These zones are prone to lose the mud and are difficult to seal. For these zones, the best drilling fluid is an inexpensive and simple mud if possible. Using oil-based mud or heavily treated water-based muds is not suggested.

Shale Problems

The most common mud-related problems encountered around the world are shale problems. Potential problems are shale swelling, dispersing or slough into the hole. Some shale problems are mechanical in nature and increasing the mud weight could be a good solution.

Some suggestions for these problems are dissolved salts like KCl for reducing shale swelling, long-chain water soluble polymers to reduce dispersion, and asphaltic

material to reduce sloughing. The effectiveness of these solutions depends on the particular shale drilled and could be different for various shale formations.

In a situation where offset experience is inadequate, lab tests on swelling and dispersive properties of the shale are often helpful in choosing a suitable drilling fluid.

Although the use of potassium, polymer, lime, gypsum and salt muds treated with asphaltic additives or a combination of these methods solves a lot of problems regarding shale drilling, no water-based mud has been universally successful.

Use oil-based muds that are adequately weighted and have high aqueous-phase salinity can eliminate issues related to shale problems. The aqueous-phase salinity should be equal to or exceed that of the water in the pore spaces of the shales drilled to prevent osmotic transfer of water into the formation (Bleier 1990).

Well Trajectory

In high-angle wells, the role of low shear rate viscosity fluids is undeniable. Special additives can be added to the mud by minimum increase in plastic viscosity and yield point, but finally results in elevated low shear rate viscosities.

Many oil-muds have good lubricity characteristics and can be treated to raise low shear rate viscosity. Additionally, some polymer muds have naturally elevated low shear rate viscosities.

Other Factors

In some areas, one drilling mud type can be much more effective in penetration rate advantages over another and approved by extensive experience. Additional factors

that may be important in selection of a suitable drilling fluid include differential sticking tendencies, formation damage concerns and special logging requirements.

Economics

The factors previously discussed are the most important factors in selecting a drilling fluid, and failure to consider them may invite loss of drilling time, loss of hole, or worse. These factors are dominating economics considerations. The remaining viable drilling fluid candidates can be subjected to a direct economic comparison. Economic considerations include the cost of base fluid, make up and main tenancy costs, mud-related disposal costs, and for oil muds, buy-back provisions and disposal costs. Other differences between systems could be cost requirements for a better solid control, or mud mixing equipment could be offset by increases in expected penetration rates or reduced mud material consumption.

There are many examples of inexpensive mud systems that are used for problem-free areas, like unweighted gel freshwater muds, lignite muds, lightly treated lignosulfonate muds and native-brine starch muds (Bleier 1990).

Completion Fluid Design Criteria and Current Technology Weaknesses

The reservoir rock characteristic at downhole conditions is a factor that should be considered in pay-zone drilling fluid design. The minerals in the formation rock and the chemical composition of the reservoir fluids should be determined. The goal is maximum well productivity and insuring of proper reservoir protection. The casing also should be set prior to drilling the pay zone section. Conventional mud is then replaced by completion fluid to start the completion process and must maintain the necessary

drilling fluid properties. A series of lab experiments must be run to see if we have any fluid/rock and fluid/fluid interaction, and also to see the residual damage caused and then determine the best treatment to remove that damage (Ezzat 1990).

Using new techniques and technologies can be effective to remove field problems such as scale precipitation while completing wells with high density brines, also damage caused by oil-based mud when followed by brine completion fluid, and fluid loss in the pay zone.

All technologies currently used have some weaknesses. Being aware of such weaknesses like long term scale inhibition for high density brines, iron solubility control, and wellbore preparation and cleaning methods can help us to mitigate the issues regarding the drilling and completion fluids.

Exposure of the fluid to reservoir rock is unavoidable during drilling and well serving operation. Completion fluid is one of the fluids that are in direct contact with the producing formation. These fluids should give us guarantees that do not destruct the rock permeability around the wellbore regardless of the reservoir type.

Concepts like the causes of formation damage and how they can be diagnosed and the relative importance of formation damage control have been discussed in many papers before. Considering these concepts can lead to successful drilling and completion of wells with minimum damage to the wells. On the other hand, not accurately determining downhole conditions or ignoring some of these conditions can cause severe formation damage problems, despite the use of highly recommended chemicals which have proved to be ideal for different reservoirs or under different conditions. Possible

reservoir rock and completion fluid reactions can then be defined and formation damage problems can be prevented.

Being aware of the potential economic impact of applying the proper formation damage control techniques, many oil companies have formed well management teams that consist of a geologist, an expert in petrophysics, reservoir and drilling engineers to define the downhole reservoir characteristics and conditions. The common goal for all these people is production optimization and reservoir protection, and they plan the well completion and implement proper procedures in the field to achieve this goal.

General Consideration of Reservoir Rock

Permeability and porosity are the primary properties that every reservoir formation should have. Clastic and carbonate rocks are common types of rocks that retain permeability and can transmit and contain hydrocarbon. Sandstones and conglomerates which contain quartz and feldspar grains with other fragments of pre-existing rocks and organic materials are classified as clastic reservoirs. Clastic rock grains are usually cemented with silica, clay minerals or carbonate. Clastic carbonates are composed of cemented fragments of shells or corals. Limestone and dolomites deposited or precipitated as calcium carbonate from fresh or sea water are classified as carbonate rocks. Dolomitization is a solution-motivated ion exchange involving calcium carbonate and magnesium chloride (Ezzat 1990). This natural process usually increases limestone porosity.

$$2CaCO_3 + MgCl_2 \rightarrow \quad CaMg(CO_3)_2 + CaCl_2 . \quad \text{.....} \quad (2.2)$$

Shales and Igneous Rocks

Sandstone reservoirs vary in texture and mineral composition and are usually inter-bedded with shale and siltstone. Such sediments were deposited in ancient oceans, lakes or rivers and streams with fluctuated or aggregated colloidal. Clay minerals are also present in carbonate rocks as partings at the bedding planes or as thin shale laminae. Volcanic ash is sometimes found in producing sands. Its effect, like that of clay minerals, is to reduce permeability when contacted with water. Clay minerals are physically unstable due to their crystal lattice and molecular structures, which permits the entry of water between the lattices and greatly change their volume. As these rocks are buried by succeeding sediments, water is squeezed out and they become consolidated by compaction (Ezzat 1990). When planning oil and gas well completions, some limitations of water- and oil-based fluids should always be remembered.

Water-based Fluids

Using water-based muds in drilling the clastic reservoirs makes the same depositional environment for these types of rocks. When exposed to aqueous fluid, these formations tend to pull back some of the water which was lost during the compaction process.

The differential pressure that the drilling operation applies to water-based mud causes the water to filter through the internal cake formed by the fine mud and drilled solids. This water reduces the relative permeability of the oil around the wellbore as a result of increasing the reservoir water saturation in this area.

Different minerals inside clays react differently with the fluids used for drilling. The longer the time contact of the clay with the fluid, the more water the clay will adsorb. Although nothing can completely stop the water adsorption to the clays, adding some water soluble salts like KCl, NaCl, NH_4Cl, $Ca(OH)_2$, etc. to the drilling fluid will slow down the reaction rate (Ezzat 1990).

The type and concentration of the salt added to the drilling fluid should be matched with the reservoir water in cation type and concentration to maintain the ionic equilibrium. If we add more salt than needed the clay may flocculate and shrink. In this situation the clay may become mobile and could cause plugging and other problems.

Factors like the pH of the filtrate and the presence of CO_2 can also cause some problems and precipitation inside the formation. Presence of CO_2 will accelerate the scale precipitation. High pH filtrate will disperse formation clays and could precipitate scale by mixing with the connate water. Filtrate pH higher than 7 could result in precipitation of salts when mixed with acidic connate water (Ezzat 1990).

Acid + Base → Salt + Water

Oil-based Fluids

In oil-based or invert emulsions, oil is the continuous phase and the mud filtrate should be all-oil under bottom hole conditions. Therefore oil-based muds are less damaging to water-sensitive formations. These kinds of fluids could be unstable for dry gas reservoirs.

Using invert-emulsion systems could be beneficial in many situations, but a lot of problems could be generated by these types of muds. Having a high concentration of

emulsifiers, these fluids may oil-wet the invaded zone and therefore decrease the effective reservoir permeability to oil. Presence of connate water could cause many issues. Connate water with low salt concentration may cause more severe emulsion blockage problems than high salinity connate water. When connate water mixes with filtrate it could form in situ emulsions and block the pores (Ezzat 1990).

Another type of drilling fluid which has been used by several operators and gives successful results is all-oil mud. The wettability characteristics of the rock may be changed slightly by all-oil filtrate but it should not oil-wet a naturally water-wet reservoir.

These all-oil systems solve the emulsion blockage problems that result from using invert-emulsion muds. Ezzat (1990) suggested a plan in field applications:

"A: Safely drill fast, stable hole with minimum possible cost

B: Stop at a point near the top of the pay zone and set casing

C: Thoroughly clean the surface system (mud tanks, pumps, manifolds, flow lines, etc.)

D: Drill residual cement and clean the wellbore

E: Displace the conventional mud with a specially designed fluid that can provide reservoir protection

F: Drill-in while maintaining optimal fluid characteristics and do not allow fluid losses into the pay zone

G: Use the same type of fluid for completion, if the zone is drilled with an oil-based fluid. In case of water-based or brine fluid, the oil-based fluid residue should be cleaned out properly without disturbing the clay minerals."

Ezzat also mentions these factors that should be considered for designing fluid formulation and to study fluid sensitivity:

"A: Reservoir rock description and thickness

B: Lithology of the pay zone section

C: Maximum reservoir pressure and static temperature expected

D: Minimum overbalanced pressure required

E: Maximum permeability, porosity and porosity description (i.e. inter-granular fracture, etc.)

F: Reservoir water chemical analysis (downhole sample is preferred)

G: Any CO_2, H_2S expected

H: Completion type, procedure and reservoir stimulation plan

I: Anticipated production rate and whether it is oil, oil and gas or dry gas

J: Reservoir rock mineralogy data such as X-ray diffraction, SEM/EDS and thin section petrography to identify:

- Clay content and clay minerals
- Minerals that can react with fluids and may form precipitate
- Plug pore throats
- Pore size distribution

K: Defined formation damage triggering mechanisms

- Chemical compatibility between reservoir connate water and fluid
- Clay stabilization
- Emulsion or water blockage
- Solid Invasion
- Change in reservoir wettability characteristics"

High Density CaCl2, CaBr2 and ZnBr2 Brines

These brine blends are used widely as completion/packer fluids. To be prepared, special skills and knowledge of the nature of these solutions is required for maintenance and reclamation of these expensive brines. In fields where well flow capacities were increased several fold as a result of utilizing clear solids-free brines, their benefits justify the cost. Few applications of $CaCl_2/CaBr_2$ have caused formation damage problems related to incompatibility with the reservoir water. Precipitation of calcium carbonate and calcium sulfate in deep hot wells has been reported in some areas. Some acid treatments such as Na_4EDTA show successful results in removing the $CaSO_4$ scale (Ezzat 1990).

CO_2 and/or formation water contamination which change the ionic equilibrium are the main problems in these wells. Extensive lab tests should be conducted simulating well conditions.

Ezzat (1990), explained that laboratory tests for $CaBr_2/ZnBr_2$ and calcium-free $NaBr/ZnBr_2$ blends were conducted at 300^oF, with and without CO_2 partial pressures, and also with and without the inorganic corrosion inhibitors. Under pressure, precipitation occurred after 22 hours. Extensive screening of all the available scale

inhibitors on the market was carried out; only one organic acidic compound was found to prevent precipitation of the scale for only 69 hours at 300°F. Serious attempts have been made in the last several years to develop an additive or a technique to stop this phenomenon.

Another problem is iron solubility in the acidic brine blends $CaBr_2/ZnBr_2$. The inorganic corrosion inhibitor proved to be capable of reducing iron solubility at high temperatures up to 550°F (273° C) to approximately 50% compared to the brine blend without the inhibitor. Iron solubility in $CaBr_2/ZnBr_2$ brines causes serious reclamation problems and expensive hazardous treatments (Ezzat 1990).

Horizontal Drilling and Completion Fluids Design Criteria

The main goal of drilling a horizontal well is to enhance productivity or injectory by placing a long distance drain-hole within the pay-zone. Field results show that production rates of the completed horizontal wells have reached several-fold higher than the vertical producing wells from these reservoirs without stimulation treatments.

The drilling fluids used in drilling long horizontal wells must satisfy the same basic functions common to all drilling muds and provide excellent reservoir protection.

Despite difficulties associated with high angle and horizontal hole drilling, developing technologies make it possible to develop these wells with a satisfactory degree of confidence.

If the drilling fluid is poorly designed or executed, difficulties such as poor hole cleaning, excessive torque or drag, wellbore instability, stuck drillstring, loss of

circulation, subsurface pressure control, poor cement jobs, and difficulties associated with running electric logs and therefore formation damage can result (Ezzat 1993).

Laboratory tests should be run to study the reservoir rock and fluid characteristics and finally select the most economic and suitable fluid formulation. Core samples should be taken from each reservoir and the effective pore size distribution and morphology of each reservoir rock should be determined to see the residual damage caused by several candidate fluids. Furthermore, awareness of drilling problems commonly encountered in similar fields can be helpful in avoiding poor drilling fluid design.

Drilling Fluid Requirement

Drilling fluids designed for vertical wells should have such characteristics as the ability to provide chemical and physical wellbore stability, control the subsurface pressure and insure effective hole cleaning. For horizontal drilling, factors like wellbore physical stability, cuttings transport, lubricity and formation damage control are very important and vital factors, which must have the most attention. Failure to fulfill any of these requirements in high-angle and horizontal wells results in costly drilling problems, increased chance of stuck drill pipe and loss of well productivity.

Wellbore Physical Stability

When the deviation angle increases, the overburden vertical stress that the wellbore should bear increases in contrast to the horizontal stress in vertical wells. To support the load imposed on the borehole wall by the in situ stresses and also to prevent hole collapse, the fluid density needed is higher than for vertical drilling. The hydrostatic

pressure must be high enough to control the subsurface pressure, but should not exceed the formation fracturing pressure to avoid splitting the formation and losing circulation (Ezzat 1993).

Cuttings Transport

Lifting off the drilled cuttings and hole cleaning is expected to be a problem in drilling high angle horizontal wells. Cuttings accumulation and the sliding back down of the cuttings on the low side of the hole when circulation stops are usually the main concerns in these wells.

Maintaining low shear rate viscosity, constant turbulent flow and circulating it into the hole prior to tripping can provide satisfactory hole cleaning and in most cases eliminate cuttings bed build-up.

Additionally, in some horizontal wells, intermittently injecting low viscosity pills followed by high viscosity slugs proved to be the best technique to insure hole cleaning. The low viscosity fluid promotes local turbulence which mechanically disturbs the cuttings bed and the high viscosity fluid sweeps the cuttings out of the hole. Successful recovery of the bottom hole assembly after being twisted off in the hole, could be a good indication that the drilling fluid characteristics and flow rates are sufficient to keep the hole clean and in good condition (Ezzat 1993).

Lubricity

One of the main problems in drilling high-angle and horizontal wells is torque and drag issues. To yield the best downhole lubricity characteristics, polymer-based low solids drilling fluid systems have been found to be the best in several fields worldwide.

The effectiveness of a drilling fluid should be verified in the laboratory using the lubricity tester. Fluid formulation with a small volume percentage of lubricant reduced the torque considerably compared to the torque generated by the same fluid without the mud lubricant.

Formation Damage Control

Detailed study of the reservoir rock characteristics is essential for tailoring a non-damaging fluid formulation. A clean non-damaging drill-in fluid could be a logical choice for drilling high-angle hole sections through the reservoir. The main objective is to complete the well in such a way as to increase productivity and recovery or injectivity. The fluid must not cause destruction of the rock permeability around the wellbore. The ideal fluid should provide maximum permeability return with minimum postdrilling cleanup (Ezzat 1993).

FILTER CAKE FORMATION, PROPERTIES AND REMOVAL METHODS

Filter Cake Formation

In many in situ hydrocarbon reservoir exploitation processes, cake filtration inherently occurs in these reservoirs. Hydraulic fracturing of petroleum-bearing rock and overbalanced drilling of wells into petroleum reservoirs are examples of the processes that cause a cross-flow filtration, which leads to a filter cake buildup over the face of the porous rock and filtrate invasion into the reservoir. In slurry with particles of different sizes, the larger particles of the slurry form the skeleton of the filter cake and the smaller particles can migrate into and deposit within the porous cake formed by the large particles. The cake simultaneously compacts due to the effect of the fluid drag as the suspension of smaller particles flow through the cake. Consequently, the porosity, permeability, and thickness of the cake vary, which in turn affects the performance of the filtration process. When slurry is applied to a filter without cross-flow, the particles are continuously deposited to form thicker filter cakes until the space available is full of the filter cake. This process is called static filtration. Dynamic filtration involves some cross flow. Therefore, the filter cake thickness varies until the particle deposition and erosion rates equal out.

A schematic of the formation of a filter cake over a surface, such as a hydraulically created fracture, is shown in **Fig. 3.1**. **Fig 3.2** shows the simplified, linear cake filtration process (Civan 2007).

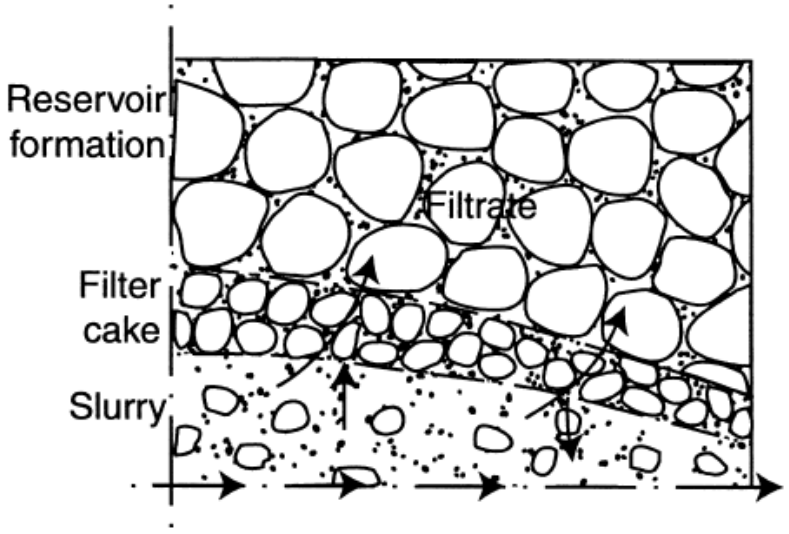

Fig. 3.1— **Filter cake buildup over a hydraulically created fracture surface (Civan 2007)**

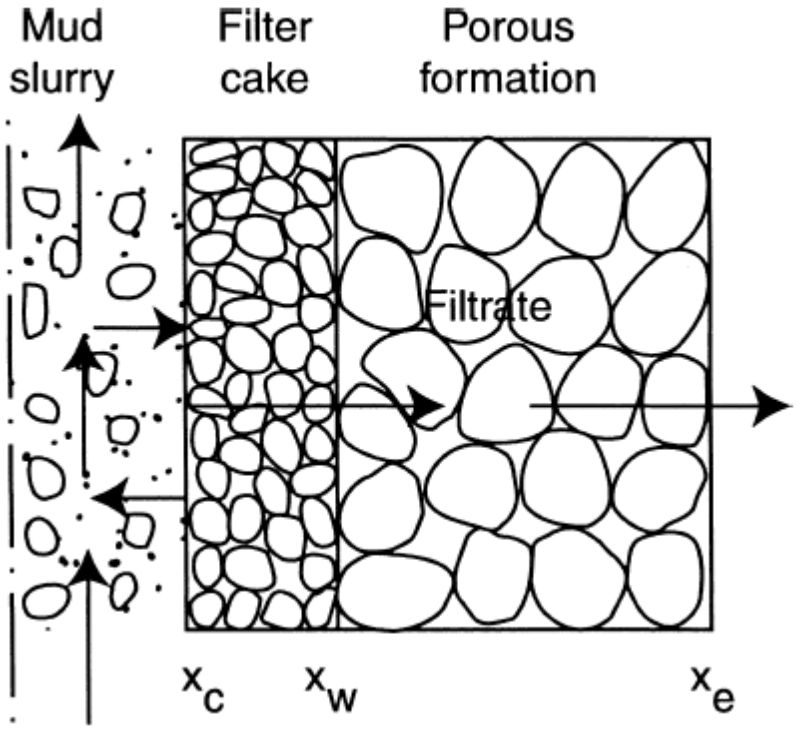

Fig. 3.2— **Linear filter cake over a flat surface of a core plug (Civan 2007)**

Factors Controlling Filtration

The most important factors and parameters that control the filtration include:

- Formation properties (permeability, porosity, pore size and structure)
- Fluid properties (cross linked or non-cross linked, power law, Newtonian or Bingham plastic, fluid additives, suspended particle size and temperature)
- Cake properties (permeability, cake compressibility, adhesive (cohesive) strength)

Formation Properties

Permeability of the formation has a very important effect on leakoff behavior. Before filter cake builds up, it is the formation that affects the leak off. During the spurt stage, high permeability causes large leak off. In cake formation, permeability is also an important factor. Low permeability rocks usually start to build a cake immediately, while high permeability rocks have a relatively longer period of spurt loss (Xie 2001).

Fluid Rheological Properties

Non-cross-linked fluids have the ability to penetrate the porous medium. Cross flow fluids have a little or very small effect on leak off behavior because non-cross-linked fluids rarely form filter cakes. Cross-linked fluids perform better in controlling fluid loss because they can build up filter cake. For power law fluids, lower n means higher shear effect.

Cake Properties

After the spurt loss stage, cake properties control the leak off behavior. Most cakes have extremely low permeability. They therefore create a large flow resistance once formed. Another factor in controlling leak off is cake compressibility (Xie 2001).

Other Factors

The preparation of the core and fluid is important for filtration experiments. Fluid preconditioning and shear history become important because shear rate can affect both fluid rheology and the rate of filter cake deposition. Temperature can also affect the fluid loss because it alters the apparent viscosity of the fluid. Higher temperatures cause lower viscosity, thus increasing the fluid loss. Long time exposure to breakers also increases the leak off.

Mud circulation is usually accompanied with drilling of wells into subsurface reservoirs, to help remove the frictional heat generated as the drill bit penetrates the rock, to provide lubrication for reduction of the frictional effects, and to transport the cuttings of the rock produced during drilling. Mud fines and filtrates invade the near-well bore formation and damage this zone. Near-wellbore mud filtrate and fine invasion during drilling operations which result in formation damage and filter cake formation are among the most important problems involved in petroleum reservoir exploitation. **Fig. 3.3** shows mud filtrate invasion in the near-wellbore formation.

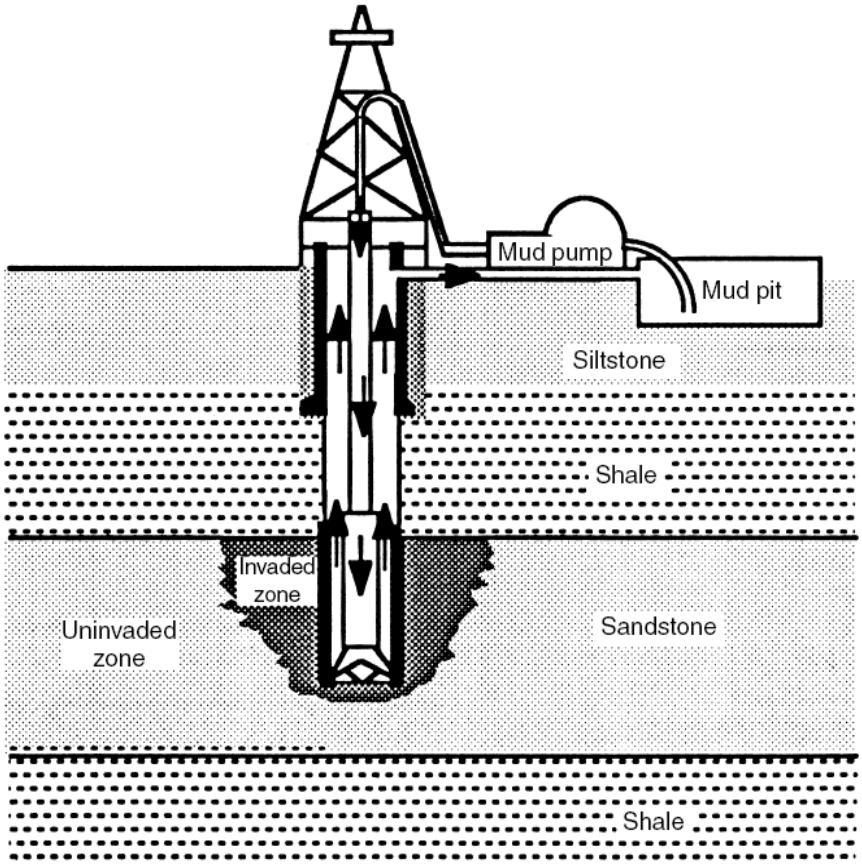

Fig. 3.3— **Mud-filtrate invasion in the near-wellbore formation (Civan 2007)**

Drilling fluids may be divided into three main groups; water-based, oil-based, or water-oil emulsion drilling fluids. Drilling muds are usually non-Newtonian fluids (Civan 2007). The type of mud can determine the depth of invasion. **Fig. 3.4** shows the depth of invasion for different types of mud. It is less damaging with oil-based muds, more with water-based muds, and moderate with emulsion muds applied to a water-wet formation.

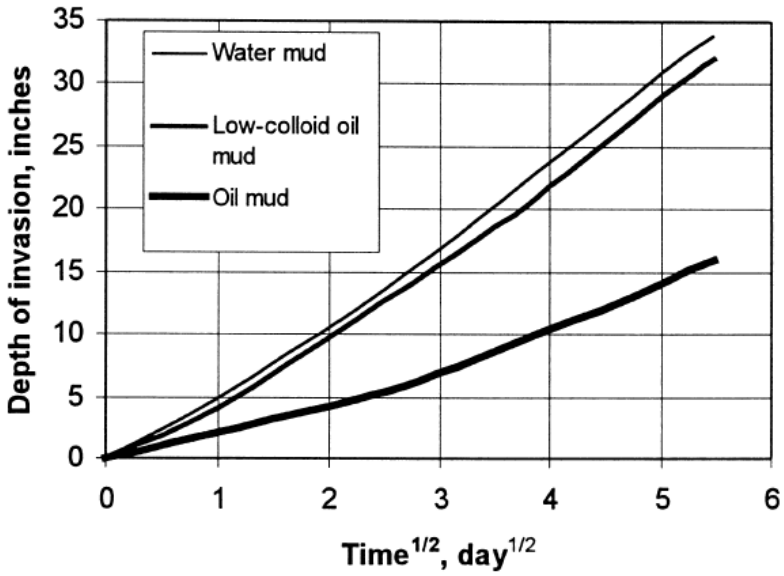

Fig. 3.4— **Depth of filtrate invasion plotted against the square root of time for different muds (Civan 2007)**

Overbalance and underbalance drilling are two ways that drilling operation of a well may be accomplished. Both techniques have certain advantages and disadvantages. The downhole pressure of the circulating mud is maintained above the reservoir fluid pressure to prevent the reservoir fluids entering into the wellbore in overbalance drilling. This method is more common in drilling jobs. Consequently, the mud filtrate and solids invade and damage the near-wellbore formation as a result of the over balance pressure forces. Eventually a protective sealing filter cake over the formation face will form. This problem can be alleviated by underbalanced drilling.

Civan states that by using unweighted drilling muds in geostatically over-pressured reservoirs, or using oil-based muds which are lighter than the water-based muds or foamed muds, the underbalance drilling can be accomplished naturally.

Therefore no mud filtrate or fines are forced into the near-wellbore formation. He explains that for high permeability, naturally fractured, and heterogeneous formations and for clay formations that are sensitive to chemicals, under balance drilling has many advantages.

Because underbalanced conditions cannot be maintained at all times during drilling, this drilling method does not completely eliminate the formation damage. Some drilling fluids can still enter the near-wellbore formation by spontaneous imbibitions, and the formation face can be damaged due to insufficient lubrication and turbulence, and inefficient cooling. For these reasons, the protective sealing filter cake formed during overbalanced drilling is still beneficial.

The mud filtrate invading the near-wellbore formation mixes with and/or displaces the reservoir fluids as shown in **Fig. 3.5** and a damage zone is created around the wellbore (Civan 2007). For accurate interpretation of the well-logs used for measurement and monitoring the properties of the near-wellbore formations and accurate estimation of the hydrocarbon content of the reservoirs, the prediction of the near-wellbore conditions, such as mud filtrate and fines invasion and distribution is important.

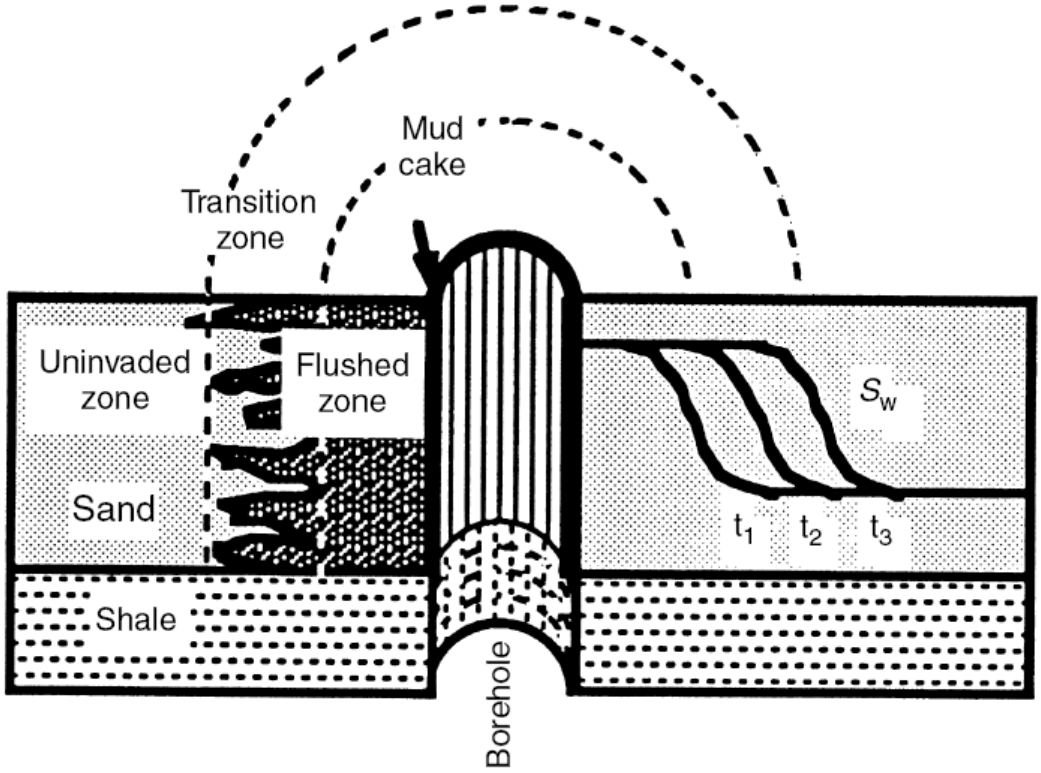

Fig. 3.5— **Schematic of the various zones and the mud filtrate invasion profiles at different times in the near-wellbore formation (Civan 2007)**

Civan (2007) states "This process is complicated by the formation of a mud filter cake and its effect on invasion by reducing the filtrate volume and the migration of fine particles into the porous formation. Simultaneously, the properties of the fluid phases in porous media, such as density and viscosity, vary as a result of mixing and interactions of reservoir fluids with the mud filtrate and fine particles."

Comparing Formation Damage of Horizontal and Vertical Wells

The demand for horizontal wells has increased recently because of advantages like maximizing reservoir exposure, targeting multiple reservoirs from a single platform,

reducing drawdown to minimize water and gas conning problems, and exploiting thin pay zones to increase reservoir drainage and productivity.

Very often for horizontal wells, water-based polymer-type mud systems are used as drilling fluids. Because of the nature of the polymers, the filter cakes formed by these types of fluids are tough and not easily degradable. Introduction of both the mud solids and polymers into the formation, the changed values of fluids saturation in the pore spaces, and the reaction between the filtrate and the pore contents and/or the matrix materials result in a reduction of the formation's original permeability.

Formation damage can potentially occur any time that solid bearing fluids enter a reservoir (Mohammed 2001). Therefore, most fluids used in different processes to drill, complete or stimulate reservoirs have the potential to cause formation damage. Some of these processes that are potentially responsible for formation damage are:

- Drilling
- Cementing
- Completions/stimulations
- Perforation
- Acidizing
- Fracturing
- Workovers
- Kill fluids
- Hot oil treatments
- Water flooding or water disposal

- Enhanced oil recovery
- Miscible flooding
- Chemical flooding
- Thermal flooding (in situ combustion/steam flooding)
- Excessive injection or production rates

Various reasons show that horizontal wells are more susceptible to formation damage than their vertical counterparts (Mohammed 2001).

Drilling fluids are longer in contact with the formation. In vertical wells, drilling may only be in the pay zone a matter of hours while in a horizontal well, the time may be measured in weeks.

Most horizontal wells are completed open hole and are not cased and perforated. Relatively shallow damage, which can be easily perforated on a standard vertical well, remains a major source of permeability reduction in many horizontal wells.

Because of the length of the well in the pay zone in horizontal wells, high drawdown is difficult to obtain in these wells. This makes it much more difficult to clean up damage due to invaded fluid or solids.

Stimulation of horizontal wells is extremely difficult and expensive. Thus once formation damage occurs, it is usually permanent in nature and effect.

Drill-in and Completion Components

Completion fluids play an extremely important role in determining the productivity of oil and gas wells. In a typical well work-over or completion operation, completion fluids will remain in contact with the productive pay zone for one to three

days. This can result in significant fluid leak off from the well to the formation resulting in potential formation damage to the near wellbore region. Maintaining a hydrostatic head in the completion fluid sufficient to prevent the flow of formation fluids into the wellbore is essential to control the well and prevent blowouts. The large wellbore pressure needed to offset the reservoir pressure often results in large fluid leak off, particularly when clear brines are used in high permeability formations. Large amounts of completion fluids lost to a reservoir can result in significant cost of makeup completion fluid (Al-Riyamy 2000).

The components used in drilling and completion fluids have been changing since the beginning of the oil industry. Water was used to be the only component in the drilling fluid to clean the bore hole by circulation in the drill pipe and through the annulus.

Careful thought was given to mud formulations after the advent of horizontal drilling technology and multilateral drilling through the pay-zone based on productivity concerns. A new class of drilling fluids was developed for use in drilling through the pay-zone. Specially formulated drilling/completion fluids for optimizing well productivity are called drill-in fluids (DIF) (Xie 2001). In addition to properties for standard drilling fluids, like providing lubricity, inhibition, solids suspension, and borehole stability, DIFs are formulated to protect producing intervals by mechanically sealing exposed pore space openings in boreholes by forming thin, tough and impermeable filter cakes, stabilizing the wellbore during completion by strengthening the wellbore, and allowing easy cleanup after drilling and completion.

Most DIFs contain solid materials such as sized calcium carbonate or sized salt. To plug the surface of a formation matrix and as weighting material to control formation pressure, solids are used as bridging agents. Viscosifiers such as biopolymers are used in drill-in fluids to provide gel strength and to improve the carrying of the drill solids to the surface. To reduce the fluid loss from the well bore to the formation, fluid loss control agents are used. The important components of the more commonly used water based drilling fluids are as follows:

- Base brines (Na, Ca, K, and cesium chlorides, bromides, halides and formates) to meet the density and formation compatibility requirements
- Sized salt/$CaCO_3$ as bridging additives
- Modified starch for controlling fluid loss
- Polymers (usually Xanthan) for desired rheology and viscosity behavior
- pH buffer for desired alkalinity requirements

The main additives of the DIF are bridging additives, fluid loss control additives, and rheology control additives.

Bridging Additive

The two most common bridging additives used in drilling fluids are sized calcium carbonate and sized salt. Sized calcium carbonate is used even more widely than sized salt. The use of calcium carbonate was proposed as a weighting material because it can be dissolved in hydrochloric acid. It is readily available as ground limestone or oyster shell. It can also be used as a substitute for barite in oil-based muds as it disperses more readily in oil than barite. Its specific gravity is between 2.6 and 2.8 which limit the

maximum density of the drill-in fluid to about 12 lb/gal. There are two advantages of using sized calcium carbonate particles in drill-in fluids (Suri 2005):

- The particles are acid soluble, which provides an option of dissolving the filter cake using acids before production
- The particles are available with different median sizes, which can be used to match the pore throat or permeability of the formation to be drilled for minimizing invasion

Proper filter cake formation, formation protection and maximizing return permeability are the factors that could determine the best design of the drilling fluid. The pores of the formation that should be sealed can affect the selection of the particle size of the calcium carbonate used as the weighting material. The largest particle size which should be used is about one half the diameter of the pore to be sealed, bridging occurring when a plurality of the carbonate particles attempted simultaneously enter the pore.

These bridging solids form the structure of the filter cake which prevents the entering of fluid and solid particles into the permeable formation. Proper filter cake design that should be considered when designing a drilling fluid to make a proper filter cake is particle size distribution, particle concentration and particle shape. Particle size distribution should be carefully controlled. The goal is to have a filter cake with maximum density, which means closest possible packing. Close packing reduces cake porosity and permeability, which reduces cake thickness and the total solids required for effective bridging (Mohammed 2001).

When the fluid is in contact with the formation, there is a spurt loss of the fluid that invades the formation. This process is continuous until solids bridge the pore throats. This bridge consists of the largest particles. Then smaller bridging solids mixed with colloidal particles layer over the top of the primary bridge. These solids make the secondary bridge. The final seal is basically a polymer film.

Formation of the drilling mud cake is different from development of a bridging film. Bridging films form very quickly and require a substantial fluid loss. In the field this process happens by the very rapid stoppage of fluid loss when pills are stopped. In the lab, the fluid spurt loss from pills as a percentage of the total fluid volume is very small. The films formed on the sand face have been observed to be persistent in adhering to the formation face (Mohammed 2001).

Fluid Loss Control Additive

The fluid contains suspended particles. These particles move with the lateral flow out of the drill hole into the porous formation. The porous formation acts like a sieve for the suspended particles. The particles will be captured near the surface and accumulate as a filter cake.

The fluid loss rate is determined by the hydrodynamic forces acting on the suspended colloids and determines the rate of filter cake buildup. An equilibrium cake thickness is achieved when no particles small enough to be deposited are available in the suspension (Mohammed 2001).

Starch is the most common fluid loss control additive used in drilling or drill-in fluids. It was the first organic polymer used in substantial quantities in mud. As other

polymers were introduced, the widespread use of starch decreased. For strongly alkaline and salt saturated muds, starch is still the most economical filtration loss control additive. However starch is subject to fermentation by many microorganisms (yeasts, molds, bacteria). To avoid this, the mud is saturated with salt or the pH is kept around 12. If mud with starch is to be used for several days, a biocide needs to be added. Starch can also break down at high temperatures and at high circulation rates. Other additives for controlling fluid loss from the well into the formation are polyanionic cellulose, sodium polyacrylonitrile and oil (Suri 2005).

Rheology Control Additive

The most common rheology control additive in drilling fluids is Xanthan. It was introduced as a drilling fluid component in the mid 1960s under the name "XC polymer" and its use has increased noticeably since 1970 (Suri 2005). It is a water soluble polysaccharide produced by bacterial action (genus xanthomonas) on carbohydrates.

Xanthan can build viscosity at lower concentrations than gum or other viscosifiers; this is an important property of Xanthan in its application to drill-in fluids. It acts as an excellent suspending agent for drill cuttings and surpasses any other polymer used in drilling or drill-in fluids. Excellent shear thinning properties with apparent viscosity markedly lower at high shear rates than that measured at low shear rates is another property of this material. Cross linking with chromic ions significantly increases viscosity. The effect of pH on viscosity in the range of 7-11 is very small. At high temperatures, it shows a negligible sign of degradation (Suri 2005).

Methods for Filter Cake Removal

In many well completions, filter cake must be removed by different methods including chemical and mechanical means. Several chemicals, known as breakers, are in common use for well clean-up, including strong mineral acids (e.g. 15% HCl), weaker organic acids, and oxidizing agents (peroxides).

Methods for removing the filter cake can be accomplished by mechanical means (scraping, jetting...) or by subsequent addition of a fluid that has some chemical as the removing agent such as an acid or base or an enzyme to dissolve at least a portion of the filter cake. Another method can be by manipulation of the physical state of the filter cake, such as by emulsion inversion (Willberg and Dismuke 2009).

The undesirable side-effects of some breakers are the highly reactive reaction rate of these chemicals. Strong acids can increase the permeability of many formations by dissolving rock minerals, but at the same time, it can cause added permeability damage if dissolved components reprecipitate. Knowledge of the design of drilling fluids and in particular how a given fluid creates a filter cake as a flow barrier between the well and the formation is a must for designing an optimal breaker (Hanssen 1999). Some of the chemical methods for removing the filter cake will be discussed here.

Emulsions

Emulsions have long been of great practical interest because of their widespread occurrence in everyday life. Emulsions are encountered in different applications in the oil industry. Emulsions have been used as drilling and completion fluids. Emulsified oil-based muds are by far the most commonly used emulsion system in oilfield.

In addition to drilling fluids, emulsions have also been used as completion fluids. The primary advantage of using oil external emulsions is that the formation is protected from the constituents of the brine in the wellbore. This can be a significant advantage when working with water-sensitive formations that can cause wellbore stability problems or loss in productivity due to interactions with the wellbore water.

Emulsions as Drilling and Completion Fluid

In 1957, Priest and Morgan developed a nonplugging perforating fluid. The principle components of the oil-in-water emulsion were an aqueous phase consisting of either sodium chloride or calcium chloride, and an oil phase consisting of diesel oil, tetrachloroethylene (not environmentally acceptable today), or a combination of both. By running laboratory tests, perforating tests and experimental field tests that contain emulsions, they demonstrate that certain emulsions serve effectively as nonplugging perforating fluids. The amount of fluid loss for an emulsion prepared with a suitable emulsifying agent was high. To reduce the fluid loss of the emulsion, each oil droplet was enveloped in a tough layer of different strengthening agents. The completion fluids prepared had no insoluble solids. The filtration properties of these emulsions were tested by an API filter cell. Its fluid loss varied from 0.5 to 9 ml at room temperature. They noticed that the flow rate into the wellbore was highest with oil-water emulsions containing calcium chloride as weighting material (Al-Riyamy 2000).

In 1974, Darley developed a process of preparing a formation-plugging material which may be readily unplugged without causing damage to the formation. The oil phase was mixed with fine, oil wet, acid soluble solid particles that help in forming an

emulsion which is stable at the temperature of the formation. The-acid soluble particles are selectively oil-wetted in the emulsion, so that they can be concentrated at the oil-water interface.

Invert emulsions are used as drilling fluids. However, due to strict environmental regulations traditional invert emulsions are not in use and the industry is using more synthetic-based muds (SBM) which are biodegradable.

Adding an acid-soluble degradable oil-in-water emulsion to the appropriate completion fluid would lower the fluid loss and increase return permeability. Also the amount of solids needed to form a filter cake would be reduced depending on the percent oil and the particle size distribution. Consequently, these low solids, low filtrate systems deposited less filter cake providing maximum removability in openhole completions. Emulsions are also good lubricants and help in freeing stuck pipes (Al-Riyamy 2000).

Micro Emulsions

In the 1950s, alcohol was added by Schulman to surfactant-stabilized oil in water (o/w) emulsions to obtain very stable homogeneous fluids that he called microemulsions. The Average droplet size of the microemulsions is 10-100 nanometers (nm), which is much smaller than conventional emulsions. The first studies of microemulsions in the oil industry were in the 1970s for enhanced oil recovery (EOR) applications (Quintero et al. 2005).

This topic became a very hot topic for research among many oil operators and universities, and they invested considerable time toward research on this topic. However the interest dropped due to the crude oil price decrease and because the technology was expensive, due mainly to the high concentration of surfactant required. Since then, the oil industry has conducted only a small amount of research on microemulsions.

Quintero (2005) states "a microemulsion is a thermodynamically stable complex fluid typically composed of a non-polar oil phase, a polar water phase, surfactant and an optional co-surfactant. They are macroscopically homogeneous and, at the microscopic level, heterogeneous, consisting of individual domains of the non-polar oil phase and polar water phase, separated by a monolayer of surfactant."

The droplet diameter of the organized phase is approximately 100 nm or less, and contains two immiscible fluids, in contrast to micellar solutions, which are considered to be one-phase fluids and may be either water or oil. The solution of microemulsions is typically clear (Quintero et al. 2005). **Fig. 3.6** shows the schematic of the micelles and microemulsions to demonstrate the difference in the structure of these two components.

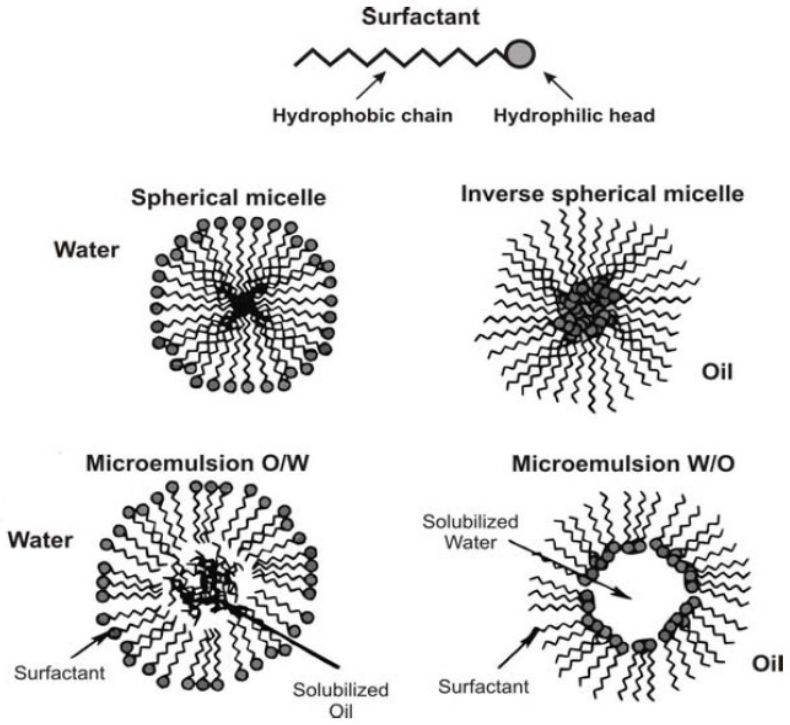

Fig. 3.6— **Schematic representation of micelles and microemulsions (Quintero et al. 2005)**

The interfacial free energy is lowered to very nearly zero by the surfactant molecules in these microemulsion fluids, which induces spontaneous microemulsification when the components are brought together. These fluids may be oil-in-water, water-in-oil, or a single-phase microemulsion with bicontinuous structure.

The water diffusion is very fast in o/w microemulsions, while the oil diffusion is low. The diffusion process is dominated by the diffusion of the oil-swollen micelles. When we have bicontinuous microemulsions, both components are expected to diffuse rapidly, having self-diffusion coefficients close to the values of the neat liquids. This

situation suggests that some continuity must exist between the water and the oil domains.

The result of Quintero's study shows that the invert emulsion system with barite treated with the single-phase microemulsion resulted in a loose, porous filter cake that may be easily displaced. This method has its own limitations.

Enzymes as Clean-up Chemicals

Enzymes are specialized proteins essential for all organisms. For some chemical reactions they are nature's catalysts, accelerating the rate of the chemical reaction. There is a difference between a catalyst and an enzyme. In contrast to chemical catalysts, most enzymes are active at mild conditions of temperature and near neutral pH. Enzymes have replaced toxic reagents and chemical catalysts in many foods, household and process uses and they are industrially manufactured. Fermentation of microorganisms is a modern industrial way of production enzymes. Amylose, a linear polysaccharide, and the related but branched amylopectin make starches, in a ratio dependent on its natural source (corn, potatoes, and other crops). The molecular weight varies by source but is usually very high: 105–109 corresponding to approx. 500-5000 monomer units. Chemically modified starches have hydroxyethyl or hydroxypropyl side-chain substituents on an unchanged backbone. **Fig. 3.7** shows (a, left): the structure of enzyme/substrate complex for α-amylase and five monomer units of a starch polysaccharide. (b, right): Reaction mechanism for degradation of amylose and amylopectin to oligosaccharides by α-amylase (Hanssen et al. 1999).

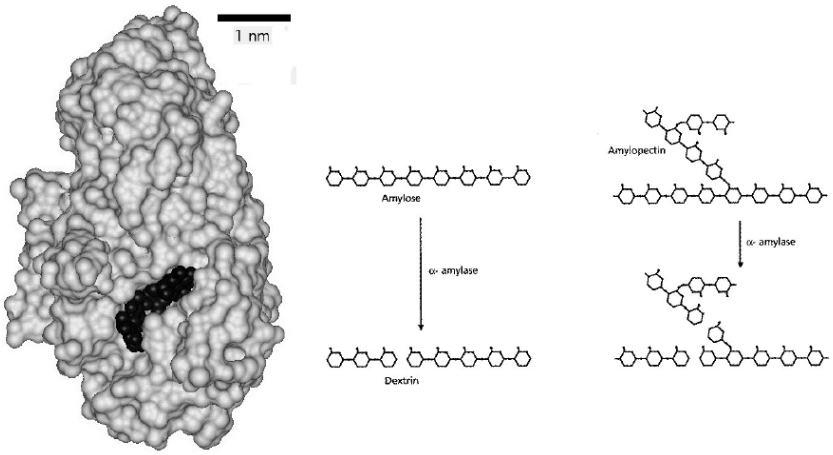

Fig. 3.7— **(a, left): Structure of enzyme/substrate complex for α-amylase and five monomer units of a starch polysaccharide. (b, right): Reaction mechanism for degradation of amylose and amylopectin to oligosaccharides by α-amylase(Hanssen et al. 1999)**

Because of their high specificity, catalytic efficiency, and excellent HSE profile, enzymes are potentially very powerful clean-up chemicals. The first field application of enzymes was to remove fracturing fluid residues. By reaching successful field experience, the use of enzymes has expanded to more demanding conditions. For better optimization of treatment to the specific mud/well/formation system to be cleaned up, two important key factors should be considered. With respect to understanding the process and the use of high-quality modern enzyme products, a margin for improvement is obvious. If by using an enzyme we have a situation of rapid, complete polymer destruction downhole, there is no need for destroying the solids, and acid post-flush treatment is not necessary. High efficiency cleanup, combined with large cost savings and avoiding the need for acid jobs make this method a good option for use as a treatment for filter cake removal (Hanssen et al. 1999).

Temperature Effect on Enzymes

An enzyme generally speeds up a reaction more as the temperature is increased. To apply this chemical correctly at oilfield conditions, the temperature dependence of enzymes must be considered. The optimum temperature for a given time and turnover requirement should be found, because reactions that deactivate the enzyme are also favored at higher temperatures.

The factors that determine the limit of the temperature for a given enzyme depend critically on the kinetics of turnover, deactivation, and transport. The maximum temperature at which it can be used is dependent on how fast the enzyme can be brought to the place where it has to do its job (Hanssen et al. 1999).

Acidic Completion Fluids

Acidic brines are sometimes used in the field to remove the filter cake. They might be effective in vertical carbonate reservoirs but they are not so in horizontal or MRC wells. The high reaction rate of the acid with the formation, especially at high temperatures, prevents effective filter cake removal in these wells.

Al-Yami (2009) describes a treatment that was done using acidic brines on field application for removing filter cake. He explains: “The hole is first cleaned out before spotting acidic brine. A 6 1/8” bit and a casing scraper were RIH to mill and clean up the hole. The hole was then cleaned with high viscosity fluid. The drill string was rotated up to 60 rpm depending on torque limitation, to remove debris from the hole. Then, filtered $CaCl_2$ brine was circulated to displace the previous drill-in fluid. The circulation is stopped when returns are clean and losses are reported. If dynamic losses are lower than

30 bbl per hour then acidic brine is spotted in the hole for 1 hour, then, the hole is circulated again with filtered brine until returns are clean and then completion is installed. If the dynamic losses are more than 30 bbl/hr then no need to pump the acidic brine."

Use of acids in long horizontal sections in not recommended because of the high volume required. Also, circulating acidic brine is not effective for sandstone reservoirs (Al-Yami and Nasr-El-Din 2009). Siddiqui and Nasr-El-Din (2005) conducted core flooding on sandstone samples and concluded that acidic brine (pH=4) is not effective in removing drilling mud filter cake (Siddiqui and Nasr-El-Din 2005).

Citric acid was used in another well, instead of HCl acid. The cleaning procedure was the same as mentioned above. The acidic brine is circulated out until a pH of 7 is obtained. But because citric acid is not a strong acid, it was not effective in removing filter cake (Al-Yami and Nasr-El-Din 2009).

In Situ Generated Acids

This breaker system of in situ generated acid technology to remove formation damage and minimize the risks with conventional breakers, is composed of special chemical components, and designed to dissolve some solid particles present in the filter cake by generating organic acid in situ. It is proposed to offer a delayed reaction, distribute uniformly among the horizontal section, and therefore, minimize the risk of corrosion (Binmoqbil et al. 2009).

Less uniform distribution of the chemical and low removal efficiency of the filter cake could result from a high reaction rate of the chemical, which may be highly reactive

to some of the sections in the targeted zone. By using drill pipe or coiled tubing, it can reach the targeted zone. A surfactant and an acid precursor are two main components of this filter cake breaker system. The function of the surfactant is to achieve the wettability alteration in the filter cake. To facilitate the reactivity of acid with very solid particles in the filter cake, surface active agents are used for altering the wettability of the oily filter cake from oil-wet to water-wet.

The acid precursor is designed to release acid with time. The acid precursor generates organic acid as a result of the hydrolysis of a carboxylic ester over a period of time when this filter cake breaker system is placed in the wellbore (Binmoqbil et al. 2009).

Al-Mojil (2007) claimed that "delayed organic acids overcome the problems and limitations associated with the conventional chemical means used to break the filter cake, namely, high reactivity of live acids. Enzyme and oxidizer attack specific polymers and do not dissolve calcium carbonate particles, the deposition of iron (III) oxide by oxidizers, and the difficulty to retard the reaction rate at high temperature for chelating agents."

In situ formic, acetic and lactic acids are current available acid precursors. These chemicals are esters which liberate organic acids when reacted with water at high temperatures.

Both lactic and formic acids have dissociation constants that are about 10 times greater than that of acetic acid. Lactic acid is similar in strength to formic acid. **Table**

3.1 gives the equilibrium constants for the acetic, formic and lactic acids at room temperature (Moajil and Nasr-El-Din 2007).

Table. 3.1— Equilibrium constants of proton transfer reactions in water at various temperatures (Moajil and Nasr-El-Din 2007)

Organic Acid	Temperature, °C					
	15	25	35	15	25	35
	pK_a [ii]			K_a [i] x 10000		
Acetic	4.76	4.757	4.757	0.174	0.175	0.175
Lactic	3.865	3.862	3.8723	1.36	1.37	1.34
Formic	3.757	3.752	3.757	1.75	1.77	1.75

i. Ka = Equilibrium constants of acids.
ii. pKa = -log(Ka)

Solubility of Calcium Salts of Organic Acids

Dissolving carbonate particles as the weighting material in the drilling fluids would be the goal of using the in situ acid generating system. However, if their calcium salts have low solubility in water, this system is less beneficial. Precursors of lactic, formic, and acetic acids were examined by Al-Moajil (2007). **Table 3.2** is a summary of the physical properties of calcium formate, acetate, and lactate. It is reported that the solubility of calcium lactate is 3.1/100 parts at 32°F, whereas the solubility is high in the case of calcium acetate, 37.4/100 parts at 32°F. The solubility of calcium formate is in between the two salts, 16.15/ 100 parts at 32°F (Moajil and Nasr-El-Din 2007).

Table. 3.2— Physical properties of calcium and ferric salts of organic acids (Moajil and Nasr-El-Din 2007)

Name	Formula	MW[i]		SG[ii]	Mp[iii]	Solubility in 100 parts		
						cold water	hot water	other reagents
Calcium Formate	$Ca(HCO_2)_2$	130.12	Colorless – rhombic (orthorhombic)	2.015	Melt at 50°C with decomposition	16.1 @ 0°C	18.4 @ 100°C	Insoluble - ethyl alcohol - ethyl ether
Calcium Acetate	$Ca(C_2H_2O_2)_2.H_2O$	176.18	White needles	1.5	Melt at 50°C with decomposition	52 @ 0°C	45.5 @ 100°C	Slightly soluble - ethyl alcohol
Calcium Lactate	$Ca(C_3H_5O_3)_2.5H_2O$	308.3	Colorless – effloresces	-	Losses 3 moles of water per formula weight at 100 °C	10.5	∞	Soluble in all proportions in hot ethyl alcohol - insoluble in ethyl ether
Iron(lll) Formate	$Fe(CHO_2)_3$	190.89	Red-yellow crystalline powder	-	-	-	-	Soluble in water, slightly soluble in ethanol
Ferric Acetate	$Fe(OH)(C_2H_3O_2)_2$	190.95	Amorphous-brown	-	-	-	-	Soluble in acid solutions -95% Ethyl Alcohol-insoluble in water
Ferric Lactate	$Fe(C_3H_5O_3)_3$	323.06	Amorphous-brown-deliquescent	-	-	Very soluble		Ethyl ether

i. MW = Molecular weight
ii. SG = Specific gravity
iii. Mp = Melting point

The solubility of calcium lactate increases with temperature. On the other hand, the solubility of calcium acetate slightly decreases with temperature, and the solubility of calcium formate is almost independent of temperature. Considering these changes in solubility is important when using these systems in the field. **Fig. 3.8** shows the solubility of calcium formate, acetate, and lactate as a function of temperature.

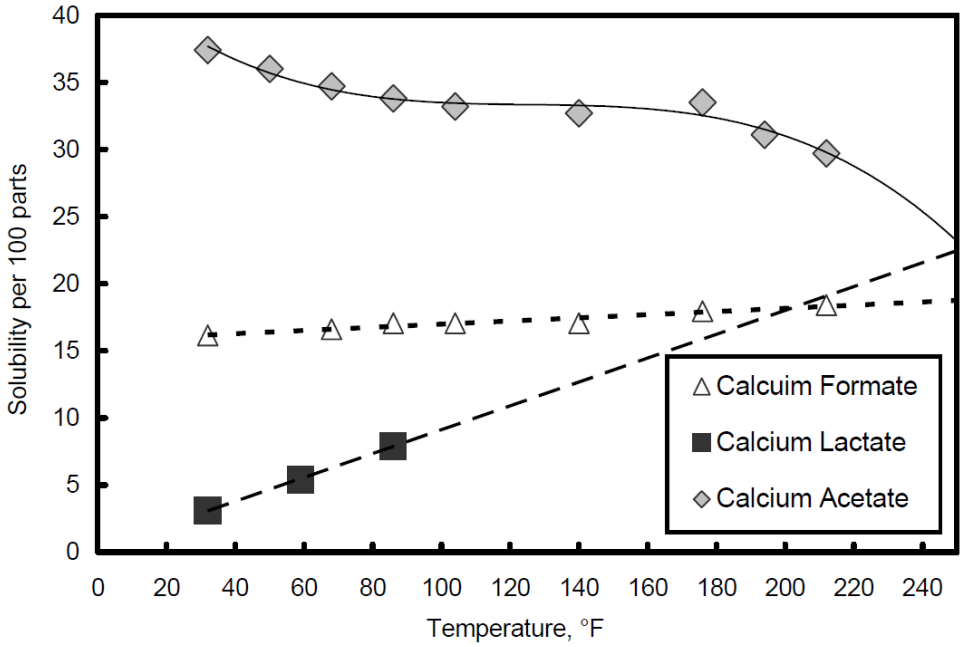

Fig. 3.8— **Effect of temperature on the solubility of calcium salts of organic acids in water (Moajil and Nasr-El-Din 2007)**

Rate of Acid Generation

The rate of acid released is expressed in terms of the half-life time of the reaction, and is mainly governed by temperature. The half life time is the time needed to generate 50% of the unreleased acid. So, in the first half life, 50% of the acid will be generated. Then, in the next half life, 25% of the acid will be generated, and so on until most of the acid is released. Theoretically, this means that if losses occur in the first half life time, a significant amount of unreleased acid will be carried into the formation (Binmoqbil et al. 2009). This may be beneficial because acid will be released deeper in the formation, and therefore, remove more mud damage.

Solids Free Drill-in Fluids as Completion Fluids

Al-Yami (2009) describes the use of solid free mud (the same invert oil base mud but with no $CaCO_3$) in a system to remove the filter cake in the field. He explains the procedure as follows: "The hole was circulated with high and low viscosity pills. Then the hole was displaced to solids free mud (same invert oil base mud but with no $CaCO_3$). We used additional salt to adjust the density we want and at least two hole volumes were circulated. After that, we installed the completion. If we have any problems while drilling or reaming then we install the completion screen first then we displace the hole to the solids free emulsion mud." For all oil drill-in fluids, methanol was used as a polar additive to achieve the required yield point, and also the organic surfactant was used to improve the oil-wetting characteristics.

Using solid-free formate brine to displace and clean formate-based drilling fluid caused only erosion to the filter cake surface and was not sufficient for complete removal. Lactic acid showed better filter cake removal of formate-based mud. But again, lactic acid has not yet been field-tested in carbonate reservoirs (Alotaibi et al. 2007).

Chelating Agents

Development of the EDTA Cleanup Treatment

Industry practices usually rely on acidic fluids for removing the filter cakes formed by drilling fluid containing $CaCO_3$. At elevated temperature (180°F), these low pH fluids react with the common oilfield alloys, which led to the evaluation of less aggressive cleanup options. Some studies, have achieved successful results using specific enzymes. EDTA has shown good results in dissolving $CaCO_3$ at near-neutral pH

(Burton et al. 2000). **Fig. 3.9** shows the molecular structure of ethylenediaminetetraacetic (EDTA).

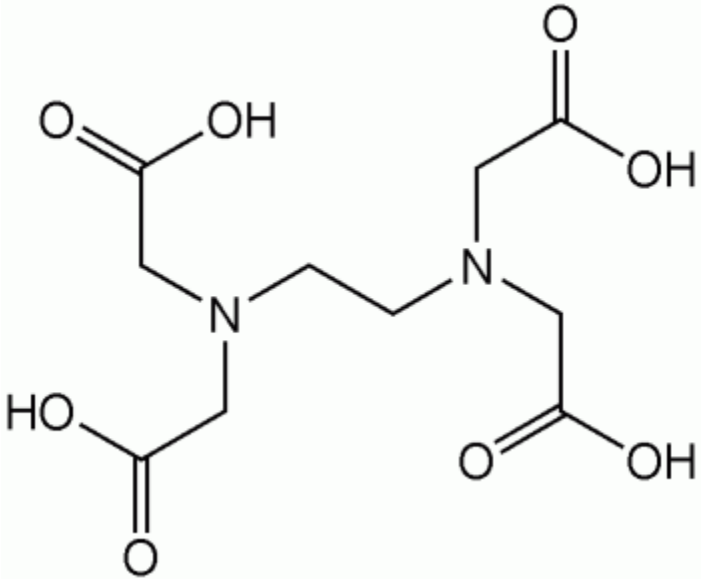

Fig. 3.9— **Molecular structure of ethylenediaminetetraacetic (EDTA)**

Burton (2000) mentions that to obtain the desired filter cake degradation without compromising the sand control screen and tubular, a single-stage treatment of enzyme with EDTA at near neutral pH was developed. Results of his experiments showed not efficient degradation by the enzyme and EDTA treatment. But addition of the ascorbic acid greatly improved the filter cake removal. Corrosion problems were also addressed in his work. Results of his tests showed that weight loss for 316-stainless steel could be limited to 0.002 pounds/ft^2 after exposure to the EDTA fluid for 6 weeks at 180°F using a corrosion inhibitor, intensifier and oxygen scavenger. His experiments show that "EDTA concentration and final pH had the greatest impact on both filter cake

degradation and corrosion. Effective dissolution of the $CaCO_3$ required approximately 50% excess EDTA on a stoichiometric basis. The optimum balance between $CaCO_3$ and enzyme activity was obtained in the PH range of 5.5 to 7.0."

All these removal methods have some requirements. They may need an additional tool or addition of another fluid to change the physical or chemical state, like changing the pH or adding a chemical. Sometimes producing a fluid that flows in the opposite direction from the flow of the fluid when the filter cake was laid down can help loosen or dissolve the filter cake, if it is a soluble salt. But these methods are not sufficiently effective, because they usually result in slow or incomplete filter cake removal. Use of a breaker for breaking the filter cake can be effective, but should be delayed by some method like esterification or encapsulation. Breakers are also often expensive and/or difficult to place and/or difficult to trigger.

Therefore, there is an obvious need for a new formulation or method that can form the filter cake from at least two components, one of which slowly reacts with water, and the second of which reacts with a reaction product to destroy the filter cake spontaneously.

In the next section, a method and composition is introduced for the drilling fluid as a self-destructive fluid loss additive to form filter cake in wellbore and subterranean formations. These fluid loss additives and filter cakes are formed from a formula of drilling fluid that has a mixture of solid acid precursor and particulate solid acid-reactive materials. Then in the presence of water, the solid acid precursor hydrolyzes and dissolves, generating acids that then dissolve the solid acid-reactive materials. This

treatment could be used in various oilfield treatments such as drilling, completion and stimulation. By using this new and novel technology there is no longer are need to use mechanical and chemical means for removing filter cake, or for injection of additional fluids. This method has great potential for use in oilfield applications.

METHODOLOGY

New Technology Using Solid-acid Precursor for Filter Cake Removal

In many field applications the presence of filter cake can help the near-wellbore region or one or more strata to prevent any undesired fluid leakoff into the porous rock at an undesirable rate during a well treatment. Such treatments include drilling, completion, stimulation (i.e. hydraulic fracturing or matrix dissolution), sand control (i.e. gravel packing, fracpacking, and sand consolidation), diversion, scale control, water control and others. Presence of the filter cake after these treatments have been completed is undesirable or unacceptable.

Fluid loss additives are added to these treatment fluids as solid insoluble materials to form the filter cake. Some fluids have polymers or cross-linked polymers as a soluble component in the drilling fluid that forms the filter cakes. Methods for removing the filter cake can be accomplished by mechanical means (scraping, jetting, etc.) or, for example, by subsequent addition of a fluid that has some chemical as the removing agent such as an acid, based or an enzyme to dissolve at least a portion of the filter cake. Another method can be by manipulation of the physical state of the filter cake, such as by emulsion inversion.

All these removal methods have some requirements. These methods are not sufficiently effective, because they usually result in slow or incomplete filter cake removal.

Therefore, a method and composition is introduced for the drilling fluid as a self-destructive fluid loss additive to form filter cake in wellbore and subterranean

formations. More particularly, this new technology is introducing a composition and method for injection of fluids containing solids that can generate filter cake in the wellbore in the drilling stage, and then generate acids for use after the filter cakes have been place.

It is necessary to mention that one of the main advantages of this technology is that it can be used in treatments rather than drilling and completion, for example this technology can be used in hydraulic fracturing treatments, in diversion treatments, in sand control treatments, in water control treatments, in matrix dissolution treatments, in sand consolidation treatments, in fracpacking treatments, and in gravel packing treatments such that delayed acid generation occurs to destroy at least part of the filter cake after the drilling, completion, fracturing, diversion or sand control treatment.

This study is about using the solid acid precursor and the solid acid-reactive material in combination as components of fluid loss additives that generate acid after their use, and react with the solid acid reactive material to destroy some or all of the filter cake after a suitable delay.

The Solid-acid Precursor

The solid acid precursor could be one or more of lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxyl-carboxylic acid. The solid acid precursor could be in any shape of solid particles or fibers or in other shapes. In the oilfield treatment composition it may be coated or encapsulated to delay the reaction rate (Willberg and Dismuke 2009).

The best sources of acid that can be generated when and where it is needed downhole, are solid cyclic dimmers under known and controllable conditions of temperature, time and pH to form the organic acids. This process of generation of delayed acid is possible by these materials that we call acid precursors in this study.

Among different possible choices introduced for use as solid acid precursors, a solid cyclic dimmer of lactic acid, lactide, which has a melting point of 95 º to 125 º C, could be a good choice. Another is a polymer of lactic acid (called polylactic acid, PLA, a polylactate, or a polylactide). Another example of a good choice for a solid acid precursor is the solid cyclic dimmer of glycolic (glycolide). It has a melting point of about 86º C. Another example is a polymer of glycolic acid (hydroxyacetic acid, PGA) or a copolymer of lactic acid and glycolic acid. All these polymers and copolymers are polyesters.

The material I have used in my experiment as a solid acid precursor is polylactic acid (PLA). It has both amorphous and crystalline grades and particle sizes from 20 microns to 150 microns. The PLA currently available has molecular weights up to about 100,000. PLA's specific gravity is 1.24g/cc and its melting temperature is around 340º F. The polymers have a high ratio of crystal to amorphous particles with different particle sizes. However any polylactide (made by any process, by any manufacturer) and material of any molecular weight of any degree of crystallinity may be used for this new drilling fluid technology. The PLA polymers are solids at room temperature and are hydrolyzed by water to form lactic acid. These polymers are insoluble in water at low temperatures but will slowly degrade into lactic acid from 100º F and up.

Rate of Hydrolysis Reaction

Factors that are important in determining the rate of hydrolysis of all these materials are governed by:

1- Molecular weight

2- Crystalinity (the ratio of crystalline to amorphous material)

3- Physical form (size and shape of the solid)

4- In the case of polylactide, the amount of the two optical isomers (the naturally occurring l-lactide forms partially crystalline polymers; synthetic dl-lactide forms amorphous polymers).

Amorphous regions are more susceptible to hydrolyze than crystalline regions. Lower molecular weight, less crystallinity and greater surface-to-mass ratio all result in faster hydrolysis. Also, change in some conditions may result in change in the rate of the hydrolysis reaction. For example, increasing the temperature, adding an acid or base, or adding a material that reacts with hydrolysis product(s) can increase the rate of the hydrolysis reaction.

The extent of the crystallinity can be controlled by the manufacturing method and ratio and distribution of lactide and glycolide for copolymers. Copolymers tend to be more amorphous despite the fact that homopolymers can be more crystalline. Polyglycolide can be made in a porous form. Some of the polymers dissolve very slowly in water before they hydrolyze. Other materials suitable as solid acid precursors are all the polymers of hydroxyacetic acid (glycolic acid).

The Solid-acid Reactive Material

The second component is a solid that reacts with the acid, called solid acid-reactive material. The solid acid reactive material is capable of at least partially dissolving in an aqueous fluid. The advantage of using solid-acid reactive material is that it promotes the formation of acid from the solid acid precursor.

Solid-acid reactive materials could be from the material usually used in oil field treatments, like calcium carbonate, aluminum hydroxide, magnesium hydroxide, magnesium oxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, or sodium zinc potassium polyphosphate glass.

Acid-soluble or acid-reactive materials are mixed with or incorporated into the solid acid precursor, such as a cyclic ester dimmer of lactic acid or glycolic acid, or homopolymers or copolymers of lactic acid or glycolic acid.

These fluid loss additives and filter cake components are added to fluids injected into the subsurface in oil field operations. The main advantage of this method is that at least a portion of the solid acid precursor slowly hydrolyzes at a controllable rate to release an acid at preselected locations and times. The acid then reacts with and dissolves at least a portion of the solid-reactive materials. The result is that at least a portion of both the solid acid precursor and the solid-acid reactive material dissolve. This is what is called the self-destructive property of the drilling mud. This property has the potential to enhance many oilfield treatments. Preferably at the end of the treatment the solid materials that initially were added to the mud are no longer present. It is only necessary that a sufficient amount of either no longer be a solid portion of the filter cake

so that the filter cake no longer forms a deleterious barrier to fluid flow (Willberg and Dismuke 2009).

How Does This New Drilling Fluid Work?

The mixtures of one or more solid acid precursors and one or more solid-acid reactive materials may be just purely physical mixtures of separate particles of the separate components. This combined mixture may be done by covering the surface of the acid-reactive material by solid acid precursor, or by melting the solid acid precursor by heating a physical mixture of the solid acid precursor and acid reactive materials, then mixing thoroughly, cooling and communicating.

When the solid-acid reactive material is completely enclosed within the solid acid precursor, the solid-acid reactive material may be water soluble. So the wettability issues should be considered while we have these combined mixtures. The uniform distribution of the components in the mixture is more preferable in all cases. For controlling the solid acid precursor hydrolysis rate and the rate and extent of dissolution of the solid-acid reactive material, the relative amounts of the components should be adjusted for any situation. The most important factors will be the temperature at which the treatment will be carried out, the composition of the aqueous fluid or fluids with which the mixture will come into contact, and the time desired for dissolution of the mixture.

The mixture of solid acid precursor and solid-acid reactive material is used as a fluid loss additive, optionally in combination with other materials, as components of filter cake forming compositions. Mixtures are added to the drilling/completion fluid to

prevent or minimize leakoff during reservoir drilling operations, but in the long term they dissolve and eventually clean up without an additional treatment step.

This fluid creates a chemically metastable filter cake that prevents fluid leakoff and formation damage during the drilling process, but readily cleans up over time. As the solid acid precursor hydrolyzes it forms an acid that attacks the carbonate or other particles, and since the solid acid precursor and carbonates or other materials are intermingled during deposition, the clean up process is uniform and extensive. In a particularly preferred situation, the acid-soluble material has a high solubility in the in situ generated acid, that is, a given amount of the acid dissolves a large amount of the acid-soluble material.

The mixture self-destructs in situ, that is, in the location where it is placed. Depending on the application of this technology, this location may be part of a suspension in the treatment fluid in the wellbore, in the perforations, in a gravel pack, or in a fracture. The application discussed here is using a solid-acid precursor and acid-reactive material as a component of a filter cake on the walls of a wellbore.

In real use, the particles may end up in other places, even though they were intended to be part of the filter cake. Particles in other places are normally undesirable because they impede the flow, so self-destruction is desired in all locations. The formation could somehow be effected by this mixture. It could be used in carbonates and sandstones. If the formation is acid-soluble, it is possible that some of the acid be consumed by the formation, so the amount of mixture, or the amount of solid acid precursor in the mixture, should be adjusted.

If the mixture is formulated so that it generates acid in excess of that required to dissolve the acid-reactive component, then the excess acid produced by hydrolysis stimulates the formation, if it contains acid-soluble material, by etching either the surface of naturally occurring fractures or the face of the formation at the wellbore.

These mixtures that generate extra acid are particularly useful in drilling and stimulation operations in carbonate reservoirs, especially in fractured carbonate reservoir. Also, an appropriate amount of buffer may be added to the fluid or to particles to counteract the effects of acid being generated by premature hydrolysis of the solid acid precursor.

The pore size distribution of the rock onto which the filter cake is to be deposited determines the needed particle sizes of the individual components of the mixture or of the combined mixture, as they relate to the use as a fluid loss additive and as filter cake former components. For the method described here, particle size distributions or size distributions may be selected as a compromise between those that are optimal for fluid loss control or filter cake formation and those that are optimal for self-destruction at the desired time and rate (Willberg and Dismuke 2009).

Delaying the Hydrolysis Reaction

The solid acid precursor or the mixture of solid acid precursor and solid-acid reactive materials may be coated to slow the hydrolysis further. Polycaprolate (a copolymer of glycolide and epsilon-caprolactone), and calcium stearate, are some examples of suitable coating, both of which are hydrophobic. Polycaprolate itself slowly hydrolyzes. The hydrolysis reaction rate is delayed by generating this hydrophobic layer

on the surface of the solid acid precursor or the mixture of the solid acid precursor and solid acid reactive materials. Another suitable method of delaying the hydrolysis of the solid acid precursor, and release of the acid, is to suspend the solid acid precursor, optionally with a hydrophobic coating, in oil or in the oil phase of an emulsion. The hydrolysis and acid release do not occur until water contacts the solid acid precursor.

The solid acid precursors or the acid-reactive material which is covered by the solid acid precursor could be in any solid shape, including but not limited to fibers, beads, films, ribbons or platelets. Coating here may refer to encapsulation or simply to change in the surface by chemical reaction or by forming or adding a thin film of another material (Willberg and Dismuke 2009).

One of the good points about this method is that for a given oilfield treatment, the appropriate solid acid precursor and solid reactive material may be selected readily from among many available materials.

Criteria for Choosing Solid-acid Precursor and Solid-acid Reactive Material

When choosing a solid acid precursor, the most important factors that should be considered are as follows:

- It should generate acid at a desired rate (after a suitable delay if needed)
- It should be compatible with and not interfere with the function of other components of the fluid

An acid-reactive material is selected that dissolves in the evolving fluid at a suitable rate and is compatible with the function of other components of the fluid.

Compatibility with Other Components of the Drilling Fluid

When mixtures of solid acid precursors and acid-reactive materials are used in fluids in treatments such as drilling, completion, and other treatments, the solid acid precursor and acid-reactive material are initially inert to the other components of the fluids, so the other fluids may be prepared and used in the usual way. Normally such fluids already contain a fluid loss additive and filter cake former, so the solid acid-precursor replace some or all of the fluid loss additive and filter cake former that would otherwise have been used. In many cases, if the fluid contains a component that would affect or be affected by the solid acid precursor or mixture of solid acid precursor and solid-reactive material (such as a buffer, or another acid-reactive material, or a viscosifier that forms or is incorporated into filter cakes), either the amount or nature of the solid acid precursor or the nature and amount of the interfering or interfered-with component may be adjusted to compensate for the interaction.

One of the other advantages of using the mixture of solid acid precursor and acid-reactive material in fluid loss additives and filter cakes is that the acid generated in the self-destruction process may break the polymeric or viscoelastic surfactant viscosifying agents and therefore play the breaker role. Acids are known to damage or destroy synthetic polymers and biopolymers used in drilling, completion and stimulation fluids. Acids are also known to damage or destroy either the micelle/vesicle structures formed by viscoelastic surfactants or, in some cases, the surfactants themselves.

However, besides the compositions and methods described in terms of producing wells for oil and/or gas, this method has other uses, for example they may be used in

injection wells (such as for enhanced recovery or for storage or disposal) or in production wells for other fluids such as carbon dioxide or water (Willberg and Dismuke 2009). In this study polylactic acid has been used as a solid acid precursor and calcite has been used as solid-acid reactive material that are added to the drilling fluid as weighting material.

Properties of $CaCO_3$ Used as Solid-acid Reactive Material

The two most common bridging additives used in drilling fluids are sized calcium carbonate and sized salt. Sized calcium carbonate is used even more widely than sized salt. The use of calcium carbonate was proposed as a weighting material because it can be dissolved in hydrochloric acid. It is readily available as ground limestone or oyster shell. It can also be used as a substitute for barite in oil-based muds as it disperses more readily in oil than barite. Its specific gravity is between 2.6 and 2.8 which limit the maximum density of drill-in fluid to about 12 lb/gal. There are two advantages of using sized calcium carbonate particles in drill-in fluids:

- The particles are acid-soluble, which provides an option of dissolving the filter cake using acids before production
- The particles are available with different median sizes which can be used to match the pore throat or permeability of the formation to be drilled for minimizing invasion (Suri 2005)

Calcite is an excellent fluid loss additive, not soluble in water even at 150° C. It has been used for years in drilling fluids to form filter cakes that are subsequently

removed with acid. Calcite, which is insoluble in water under these conditions, accelerates the rate of hydrolysis and itself dissolves in the generated acid.

Properties of Polylactic Acid as Solid-acid Precursor

Recently, the application of bio-renewable materials as substitutes for petroleum-based feedstocks is growing. This is directly related to the increase in oil price and the search for other alternative products.

Lactic acid (2-hydroxypropionic acid) is the major building block for the biorenewable economy. It is α-hydroxy acid containing both a hydroxyl and carboxylic acid functional group. Lactic acid is useful in the food (as an additive and preservative), cosmetic, textile, and leather industries. Lactic acid can be created by fermentation of carbohydrate monomers or by a chemical route, but using the fermentation route to form lactic acid has become more common since about 1990.

Among all polymers, PLA is one of the few that the properties and structure of which can be changed by polymerizing a controlled composition of the l- and d-isomers to achieve high molecular weight amorphous or crystalline polymers.

Mixture with alcohols like methanol and ethanol can produce esters of lactic acid, which are useful as environmentally benign solvents. Lactic acid esters are biodegradable and non-toxic. Lactic acid esters have outstanding solvent properties, which make them as an excellent alternative to substitute for halogenated solvents in a wide range of uses (Vu et al. 2005).

Hydrolysis Reaction

Hydrolysis of esters of lactic acid is particularly similar to the hydrolysis of any other esters. Thus it is catalyzed by acid (hydrogen ions) or by alkali (hydroxyl ions). Hydrolysis can also occur by reaction with just water, but this type of hydrolysis results in acid catalyzation by the lactic acid firstly liberated (Holten et al. 1971).

In summary, a particular advantage of these materials is that the solid acid precursors and generated acids are non-toxic and are biodegradable. The solid-acid precursors are often used as self-dissolving structures.

EXPERIMENTAL WORK, RESULTS, AND DISCUSSION

Experimental Setup and Procedure

Material

The drilling fluid used to perform the tests was lab sample of gel/polymer water-based mud. The composition of the drilling fluid is given in **Table 5.1**. The mud uses $CaCO_3$ (calcite) as weighting material. Calcite is known to be an excellent fluid loss additive. It has some good properties that are useful for this new technique, for example calcite is not soluble in water, even at 150° C. Calcite has been used for years in drilling fluids to form filter cakes that are subsequently removed with acid. Its specific gravity is between 2.6 and 2.8, which limits the maximum density of drill-in fluid to about 12 lb_m/gal.

Another component in the drilling fluid is Rev-Dust. Rev Dust is a simulated drill solid (typically a low-reactive clay, SG=2.6-2.7) to simulate a field drilling mud. Density and rheological properties of the mud were measured in the lab.

Table. 5.1— Formulation of gel/polymer water-based mud

Material	Quantity (per bbl)	Units
Water	319	lb
Viscosifiers/API Filtrate control	18	lb
HT/HP Filtrate Control	0.25	lb
Secondary Thinner	4.0	lb
Alkalinity Agent	0.6	lb
Calcium Carbonate	28	lb
Rev Dust	27	lb

A Hamilton mixer was used to prepare the samples. Drilling fluids were mixed by using the Multi-mixer Model 9B as shown in **Fig. 5.1.** The average speeds of the impellers were 11300 rpm.

Fig. 5.1— Multimixer model 9B

Density

The density of the fluid was measured by Mud Balance (Baroid Mud Balance Model 140, **Fig. 5.2**). It should be calibrated frequently with fresh water. Fresh water should give a reading of 62.3 PCF at 70ºF.

Fig. 5.2— Mud balance

Procedure

- Put the instrument in a level position
- Fill the clean, dry cup with fluid to be tested; we should make sure that some of the fluid is expelled through the hole in the cap to free trapped air
- Wash or wipe the fluid from the outside of the cup. Put the beam on the support and balance it by moving the rider along the graduated scale. The beam should be in the horizontal direction and the bubble in the center line

Measuring Rheological Properties

Fann 35 Viscometer (**Fig. 5.3**) was used to measuring the rheological properties of the fluid.

Fig. 5.3— Fann 35 viscometer

Procedure

Yield Point & Plastic Viscosity Measurements

- Place a sample in a suitable container and immerse the rotor sleeve exactly to the inscribed line
- Set the temperature to 120°F
- With the sleeve rotating at 600 rpm, wait for the dial reading to reach a steady value. Record the dial reading for 600 rpm
- Shift to 300 rpm and wait for the dial reading to come to a steady value. Record the dial reading for 300 rpm
- Repeat the experiment for 6 rpm and 3 rpm (optionally for 100 and 200 rpm)
- The plastic viscosity (PV) in centipoises equals the 600 rpm reading minus the 300 rpm reading

- The yield point (YP) in $Ib_f/100\ ft^2$ equals the 300 rpm reading minus the plastic viscosity. The temperature of the sample should be 120°F

Gel-Strength Measurement

- Place the fluid sample in position as in the procedure for plastic viscosity and yield point measurement
- Stir at 600 rpm for a while
- Allow the fluid to stand undisturbed for 10 seconds. Then start stirring at 3 rpm. The maximum reading attained after starting rotation at 3 rpm is the initial gel strength
- Again stir the fluid sample at 600 rpm for a while and then allow the fluid to stand undisturbed for 10 minutes, then put it in 3 rpm, The measurement at the maximum reading is 10-minutes gel strength in $Ib_f/100\ ft^2$

HPHT Fluid Loss Cell

A HP/HT fluid loss cell, **Fig. 5.4**, was used to determine the efficiency of removing the filter cake by using water as cleaning fluid. This cell was selected because of its ability to simulate the downhole conditions. The formation face was simulated by inserting a ceramic disc of a known permeability into the cell. The dimensions of a typical disk were 2.5 inches in diameter and 0.25 inch in thickness. The mean pore size of the ceramic disk was nearly 10 microns. All ceramic disks were saturated in water for at least 24 hrs.

A static test was performed to assess the efficiency of washing fluid to remove the filter cake present on the disk. The test was carried out at temperatures between 170°F to 330° F.

300 psi differential pressure was used in all experiments to stimulate overbalance pressure in downhole condition.

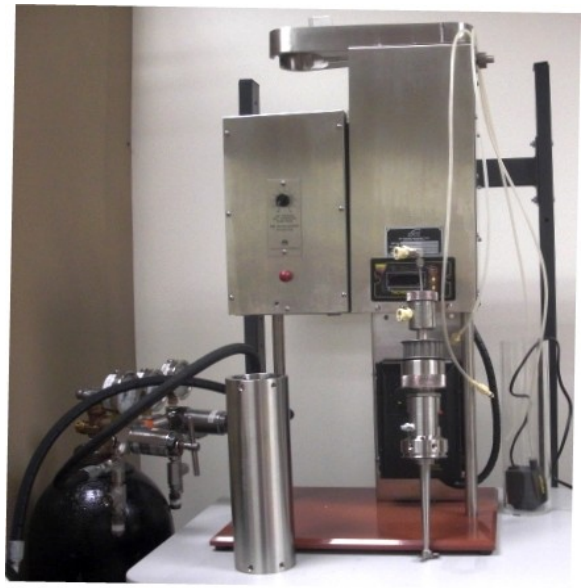

Fig. 5.4— HPHT filter press

Procedure

- Lubricate the O-rings. Preheat the heating jacket to a little bit above selected test temperature
- Load the cell with the fluid sample, take care not to fill the cell closer than ½ inch from the top
- Put the cell inside the equipment; make sure it is completely inside

- Place the cell into the heating jacket with both top and bottom valves closed. Transfer the thermometer into the thermometer well
- Place the pressure units on the valves and lock in place. Apply 300 psi differential pressure to the fluid while heating to the selected temperature
- Record the filtrate volume every minute. Total time of reading is 30 min
- At the end of the test close both valves, back the T-screw off, and bleed pressure from both regulators

Analytical Tests

After the drilling fluids and filter cakes were examined with the HT/HP filter press, a chemical analysis of the return cleaning solution was conducted. Atomic absorption spectroscopy (AAS) was used to measure the concentration of calcium in returned cleaning fluid samples for different sets of experiments. Also, the density of various solutions at room temperatures and 1 atmosphere was measured using a Paar densitometer model DMA-35, (**Fig. 5.5**). The pH of the samples was measured using ExStik EC500 pH meter (**Fig. 5.6**).

Fig. 5.5— Density meter

Fig. 5.6— pH meter

Atomic Absorption

Beaty (1993) explained the atomic absorption process "The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which

is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyzed element present can be made. The use of special light sources and careful selection of wavelength allow specific quantitative determination of individual elements in the presence of others".

"The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp (Beaty and Kerber 1993). The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals." **Fig. 5.7** shows the atomic absorption process.

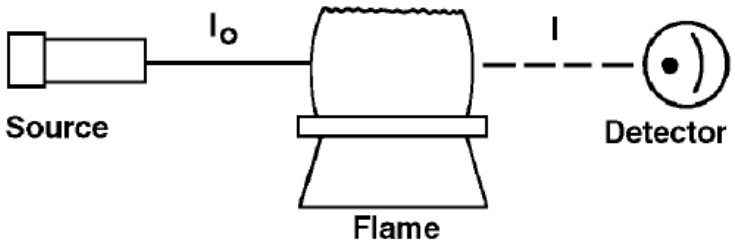

Fig. 5.7— The atomic absorption process (Beaty and Kerber 1993)

We have used atomic absorption spectroscopy (AAS), Perkin Elmer analyst 700, to determine the calcium concentration in the return cleaning solution. **Fig. 5.8** is a picture of the equipment used for our experiments.

Fig. 5.8— Atomic absorption equipment

Procedure

- Make sure that the ventilation is working
- Open the air tank and adjust air-pressure
- Open acetylene tank and adjust acetylene pressure
- Switch the machine on
- Go to computer and select the method
- Go to the hollow cathode lamp and chose the element (Ca)

- Light the lamp and leave it 20 min, to be warmed up
- Adjust the burner head vertically and horizontally
- Ignite the flame and select auto zero
- Aspirate deionized water and select auto zero
- Aspirate the calibration blank (2% HNO_3) and select auto zero
- Analyze the standard one by one
- Go to calibration and check the linearity of the standard and the correlation coefficient value
- If everything is right analyze samples
- Check every 5 samples by aspirating the calibration blank or the chosen re-slope standard
- Go to results and watch your data
- Save the method and close the winlab program window after closing air and acetylene and bleeding them from the pipes. Your results will be in mg/L
- If any samples are deviated from the range of the standard curve (0-25.34 mg/L) make the appropriate dilution and reanalyze them again

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electron microscopy that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

I have used an FEI Quanta 600 (**Fig. 5.9**) to see the morphology and component elements of a sample of removed filter cake. Experiments were performed with FEI Quanta 600 field emission scanning electron microscopy (FESEM) equipped with a Schottky field emission gun. A conventional Everhart-Thornley detector and Oxford energy dispersive x-ray spectroscopy (EDS) system attached to the FESEM were used for imaging and elemental analysis. After the area of interest was found and recorded, the EDS spectrum from a spot or local region of the area was collected at a 20 kV, accelerating voltage with a stationary electron probe. The spectrum was analyzed with the INCA microanalysis suite to identify component elements.

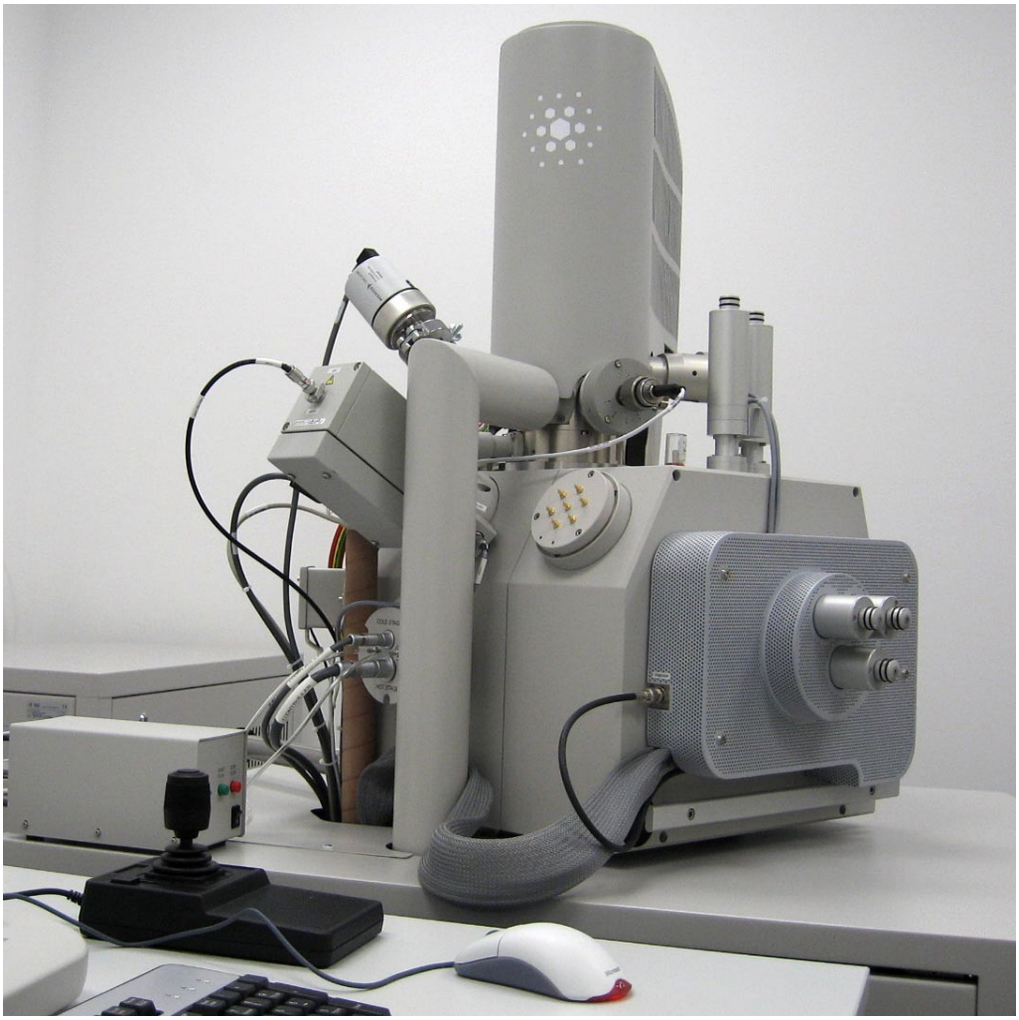

Fig. 5.9— FEI Quanta 600

X-Ray Diffraction (XRD)

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and diffracts into many specific directions. From the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the

crystal can be determined, as well as their chemical bonds, their disorder and various other information.

I have done XRD by using a Bruker D8 Advance Powder X-ray Diffractometer (**Fig. 5.10**) on a sample of removed filter cake to see the elements and compounds in the sample. The Bruker D8 Advance is a conventional powder X-ray diffractometer. In this design, the sample is held horizontally allowing the use of a number of different sample holders.

The sample was placed in the sample holder of a two circle goniometer, enclosed in a radiation safety enclosure. The X-ray source was a 2.2 kW Cu X-ray tube, maintained at an operating current of 40 kV and 40 mA. The X-ray optics was the standard Bragg-Brentano para-focusing mode with the X-ray diverging from a DS slit (1 mm) at the tube to strike the sample and then converging at a position sensitive X-ray detector (Lynx-Eye, Bruker-AXS). The two-circle 250mm diameter goniometer was computer controlled with independent stepper motors and optical encoders for θ and 2θ circles with the smallest angular step size of 0.0001^{o} 2θ. The software suit for data collection and evaluation is windows-based. Data is collected via an automated COMMANDER program by employing a DQL file. Data is analyzed by the program EVA.

Fig. 5.10— Bruker D8 advance powder x-Ray diffractometer

Results and Discussion

The drilling fluid used to perform the tests was lab sample of gel/polymer water-based mud. **Table 5.2** gives the properties of the mud.

Table. 5.2— Density and rheological properties of the gel/polymer water-based mud

Property	Value	Units
Density	68	lb_m/ft^3
Plastic Viscosity	10	cp
Yield Point	6	$lb_f/100\ ft^2$
Gel Strength (10 sec) (10 min)	4 6	$lb_f/100\ ft^2$

The purpose of this research is to develop a mixture of solid acid precursor and solid acid-reactive material that can be used as fluid loss additives, optionally in combination with other materials, as components of filter cake forming compositions. Mixtures are added to the drilling fluid to prevent or minimize leakoff during reservoir drilling, but in the long term they dissolve and eventually clean up without an additional treatment step.

This fluid creates a chemically meta-stable filter cake that prevents fluid leakoff and formation damage during the drilling process but readily cleans up over time. As the solid acid-precursor hydrolyzes it forms an acid that attacks the carbonate or other particles and since the solid acid precursor and carbonates are intermingled during deposition, the clean up process is uniform and extensive. The first step was to develop such self-destructing drilling fluid. The material I have used in my experiment as solid acid precursor is solid polylactic acid (PLA) and $CaCO_3$ (as weighting material) to function as solid-acid reactive material.

Developing Self-Destructing Drilling Fluid

The First step in this project was to develop a drilling formula that has the properties described above. The assumption here was to keep the density of the drilling fluid constant. By doing some material balance equations and replacing some simulated solids in the original drilling fluid formula with some solid polylactic acid and adding some more calcium carbonate to reach the desired density, we developed the self-destructing drilling formula. The composition and properties of the new self-destructing drilling formula are given in **Table 5.3** and **Table 5.4**.

Table. 5.3— Formulation of self-destructing water-based mud

Material	Quantity (per bbl)	Units
Water	319	bbl
Viscosifiers/API Filtrate control	18	bbl
HT/HP Filtrate Control	0.25	bbl
Secondary Thinner	4.0	bbl
Alkalinity Agent	0.6	bbl
Calcium Carbonate	38	bbl
Rev Dust	10	bbl
Solid Acid Precursor	21	bbl

Table. 5.4— Properties of the self-destructing water-based mud

Property	Value	Units
Density	69	lb_m/ft^3
Plastic Viscosity	11	cp
Yield Point	8	lb_f /100 ft^2
Gel Strength (10sec) (10 min)	3 5	lb_f/100 ft^2

Fig. 5.11 shows the comparison between the original gel/polymer water-based mud and the newly developed self-destructing mud. Plastic viscosity and yield point can be read from the graph. **Fig. 5.12** shows the viscosity of the gel/polymer water-based mud in comparison with the new self-destructing mud. Figures show similar behavior of these two drilling fluids. Properties of these two muds such as plastic viscosity and yield point and gel strength are very close.

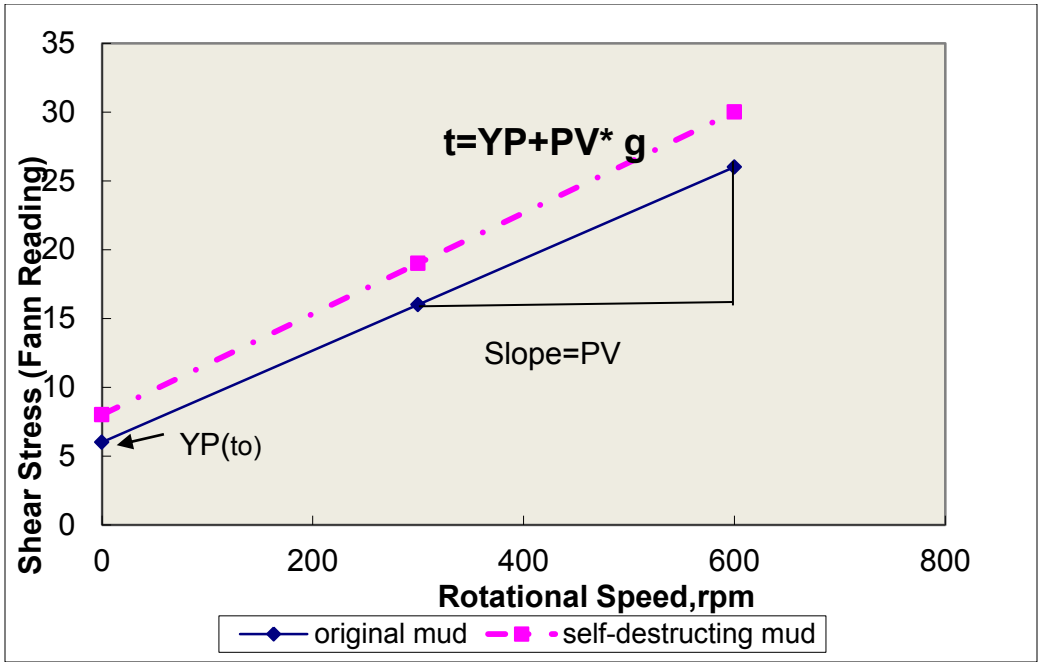

Fig. 5.11— Comparison of rheological properties of self-destructing mud with original gel/polymer water-based mud

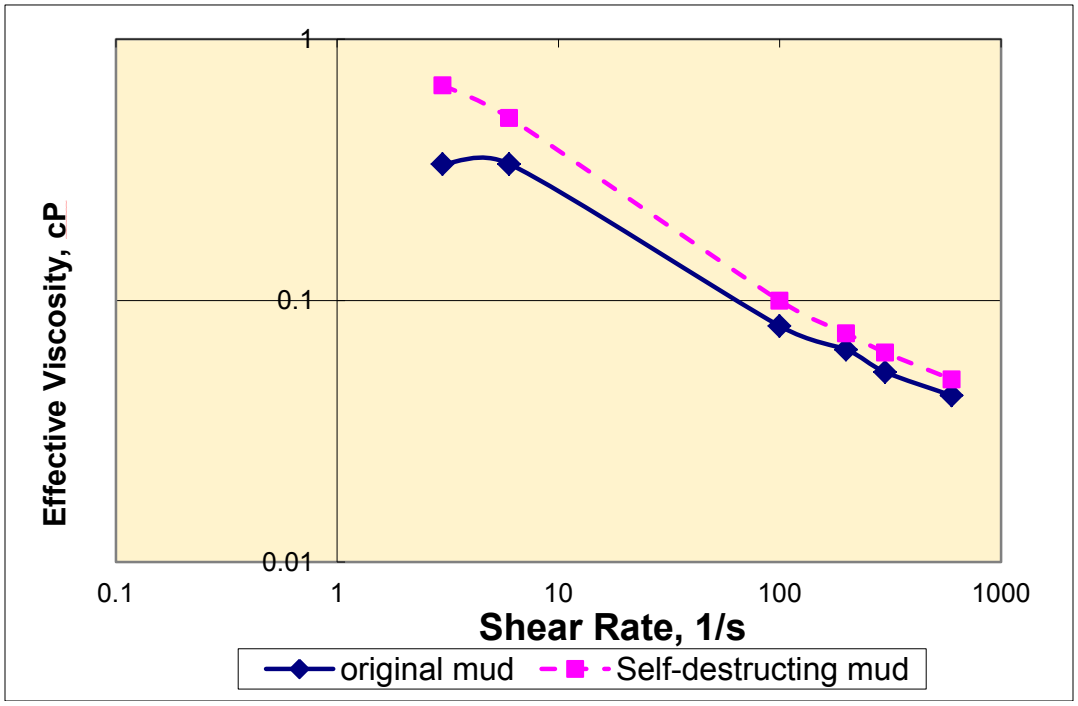

Fig. 5.12— Viscosity behavior of the gel/polymer water-based mud by changing shear rate

Solid-acid Particle Size Effect

The pore size distribution of the rock onto which the filter cake is to be deposited determines the required particle size of the individual components of the mixture or of the combined mixture, as they relate to the use as a fluid loss additive and as filter cake former components. For the method described here, particle size distributions may be selected as a compromise between those that are optimal for fluid loss control or filter cake formation and those that are optimal for self-destruction at the desired time and rate.

The most important factors which should be considered for choosing a solid acid precursor are that it should:

- Generate acid at the desired rate (after a suitable delay if needed)
- Be compatible with and not interfere with the function of other components of the fluid

To find the optimum particle size distribution of the two main components of the drilling fluid (polylactic acid as solid acid precursor and calcium carbonate as solid-reactive material), two sets of experiments have been done. The particle sizes that were available for polylactic acid were 20 microns, 50 microns and 150 microns. The solid particles of calcium carbonate were fine (around 50) and 150 micron particles. The first set of experiments was to find the best size for solid acid particles. The calcium carbonate was chosen to be fine particles. Three drilling fluids were prepared that had the same components except for the size of solid-acid particles.

D.F (f/150) is a drilling fluid that has fine particles of calcium carbonate and 150 micron particle size of solid acid. In the same manner, **D.F (f/50)** is a drilling fluid that has fine particles of calcium carbonate and a 50 micron particle size of solid acid. **D.F (fine/20)** is fluid with fine calcium carbonate and a 20 micron particle size of solid acid. Rheological properties of these fluids are given in **Table 5.5.**

Table. 5.5— Rheological properties of drilling fluids with different solid-acid particle sizes

Property	**D.F(f/150)**	**D.F(f/50)**	**D.F(f/20)**	**Units**
Density	69	69	69	lb_m/ft^3
Plastic Viscosity	11	13	11	cP
Yield Point	8	12	15	$lb_f/100\ ft^2$
Gel Strength (10 sec)	3	4	2	$lb_f/100\ ft^2$
Gel strength (10 min)	5	7	6	$lb_f/100\ ft^2$

Fig. 5.13 shows effective viscosity of these drilling fluids at different shear rates. It shows different behaviors of drilling fluids with different solid acid particle sizes.

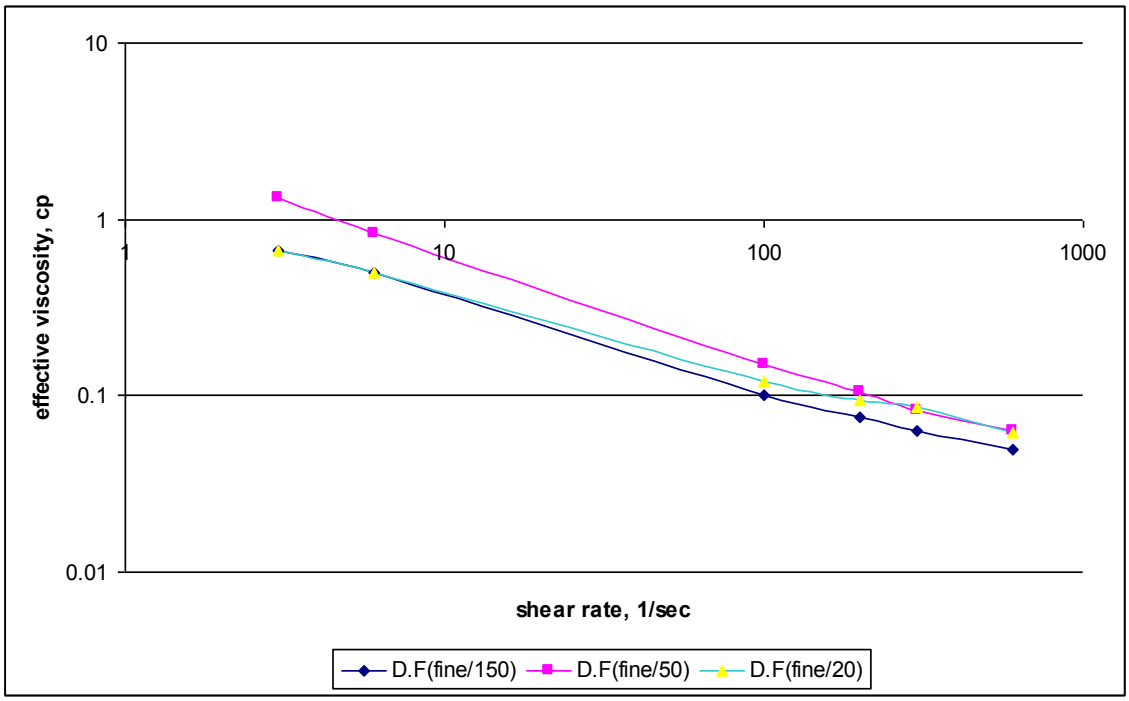

Fig. 5.13— Different behavior for three drilling fluids with different solid acid particle sizes

HT/HP fluid loss experiments have been done on this set of drilling fluids. All experiments have been done at a temperature of 260° F and 300 psi differential pressure. First, the filter cake was formed at this temperature and pressure. The filtrate was collected over a 30 minutes interval and the result of the fluid loss experiment is given in **Fig. 5.14**. It shows that the fluid loss was less damaging for drilling fluid that has solid acid particles of 150 microns.

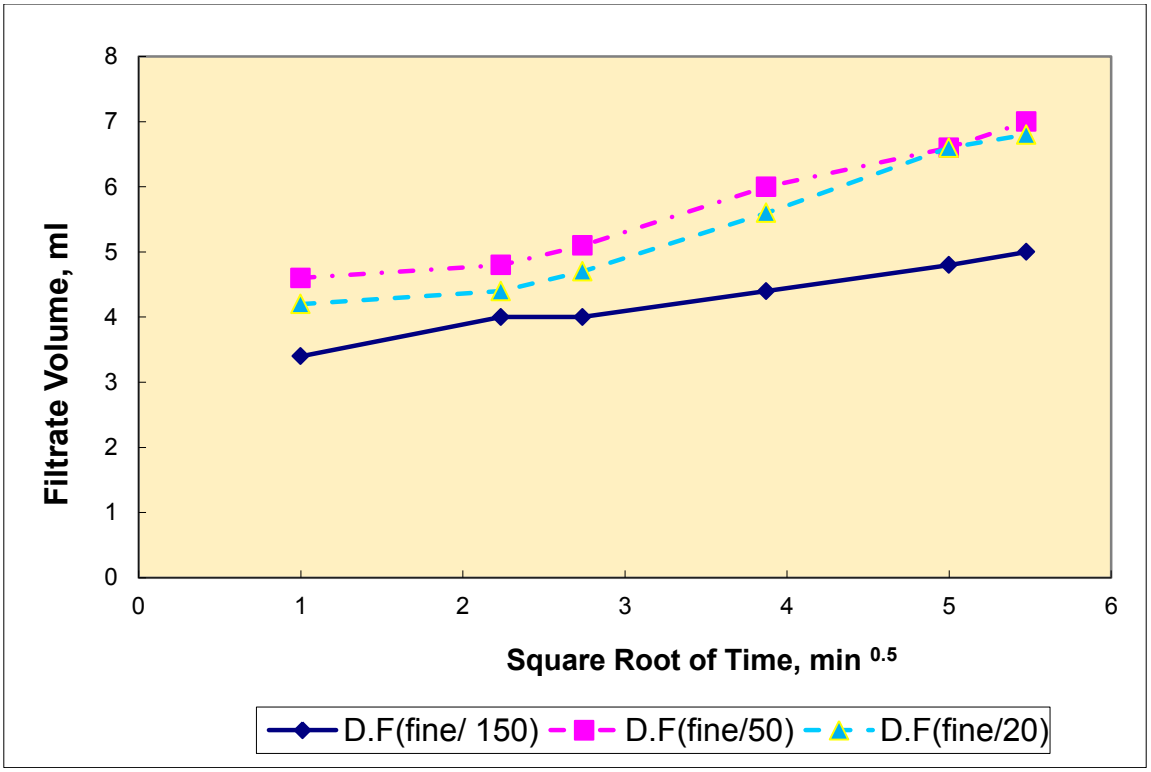

Fig. 5.14— Comparison between drilling fluids with different solid acid particle sizes shows less damaging fluid when we have 150 micron solid acid with fine calcium carbonate particles

Filter cakes were then placed in the HT/HP fluid loss again to be in contact with water at the same condition of temperature and pressure. The solid polylactic acid that now is part of the filter cake will start to hydrolyze at high temperature and after enough soaking time. It starts to dissolve the calcium carbonate particles in the filter cake and finally no filter cake remains on the ceramic disk. Soaking time for all experiments was 20 hours.

Fig. 5.15 shows the filter cakes and remained filter cakes after 20 hours soaking in water at 260° F and 300 psi differential pressure.

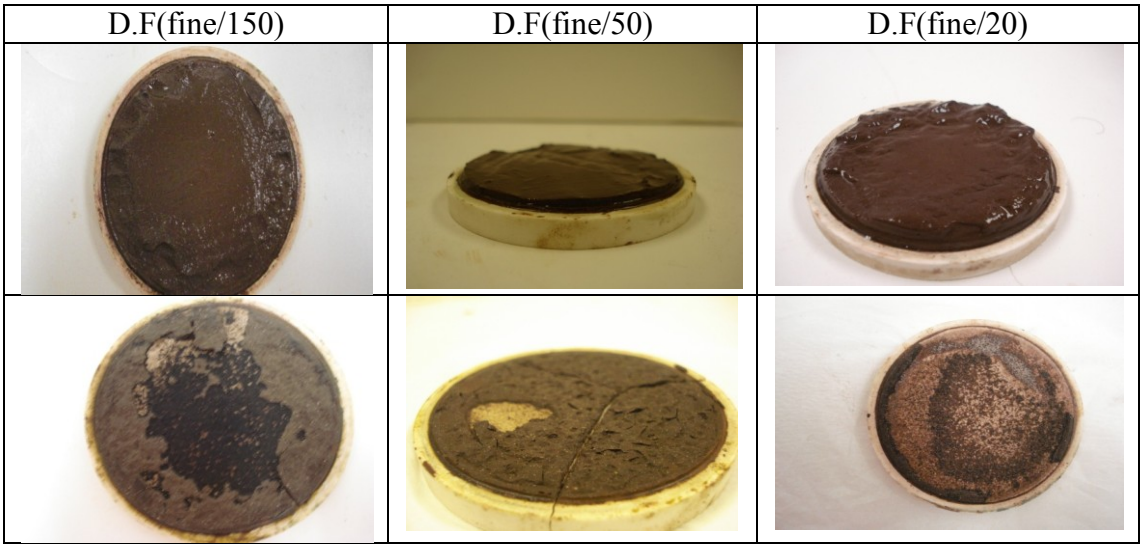

Fig. 5.15— Filter cakes and remained-filter cakes after 20 hours soaking in water at 260° F and 300 psi differential pressure

Efficiency of Filter Cake Removal

Efficiency of removing the filter cake is done by measuring the weight of the ceramic disk after saturation in water for at least 24 hours. Then after forming the filter cake at high temperature and high pressure conditions, the weight of the ceramic disk should be measured again. After soaking in the cleaning solution, the weight of the filter cake is measured. Efficiency is calculated by this formula based on weight differences before and after treatment.

$$Efficiency = \frac{(W_{Disk+\ filtercake}) - (W_{Disk+\ Remained-\ filtercake})}{W_{Disk+\ filtercake} - W_{Disk}} \quad \text{..... (5.1)}$$

Table 5.6 gives the efficiency of filter cake removal for these three drilling fluids with different solid acid particle sizes.

Table. 5.6— Efficiency of filter cake removal for drilling fluid with different solid-acid particle sizes

Measured Weights (gram)	D.F(fine/150)	D.F(fine/50)	D.F(fine/20)
W_{Disk}	47.55	49.55	47.92
$W_{Disk+\ ìltercake}$	58.53	56.95	59.52
$W_{Disk+\mathrm{Re}moved-\ ìltercake}$	49.75	53.23	48.52
Efficiency (%)	80	49	95

This set of experiments showed that the best particle size distribution to make a self-destructing filter cake is when fine particles of calcium carbonate are used as weighting material in a drilling fluid with 150 micron solid acid precursor. This size distribution shows low invasion of the drilling mud to the formation and therefore less damage to the formation compared to the two other drilling fluids. Also, the removing efficiency of the filter cake is satisfying and most of the filter cake can be removed from the wall of the well at high temperature and high pressure operation conditions.

Calcium Carbonate Particle Size Effect

Another main component of the self-destructing drilling fluid formula is the calcium carbonate that functions as solid-acid reactive material in the drilling fluid. Calcite is known to be an excellent fluid loss additive. It has some good properties that are useful for this new technique. For example, calcite is not soluble in water, even at 150° C. Calcite has been used for years in drilling fluids to form filter cakes that are subsequently removed with acid. A set of experiment has been done with 150 micron

particle sizes of calcite. For comparison with the previous result, the best drilling fluid from the previous set of experiments, which was D.F (fine/150), is compared at the same figure with the samples here to find the best particle size distribution for the self-destructing drilling fluid.

HT/HP fluid loss experiments have been done on this set of drilling fluids. All experiments have been done at a temperature of 230° F and 300 psi differential pressure. First, the filter cake was formed at this temperature and pressure. The filtrate was collected over a 30 minutes interval and the result of the fluid loss experiment is given in **Fig. 5.16**. Drilling fluids used in this set of experiments are **D.F (150/150)**, which has 150 micron calcite particles and 150 micron solid acid particles. **D.F (150/50)**, with 150 micron calcite and 50 micron solid acids, and **D.F (fine/150)** which has fine (around 50 micron) calcite particles and 150 micron solid acid. It shows that the fluid loss was less damaging for drilling fluid that has fine (around 50 micron) calcite particles and solid acid particles of 150 microns (D.F (fine/150)). This result confirms the results from the previous part.

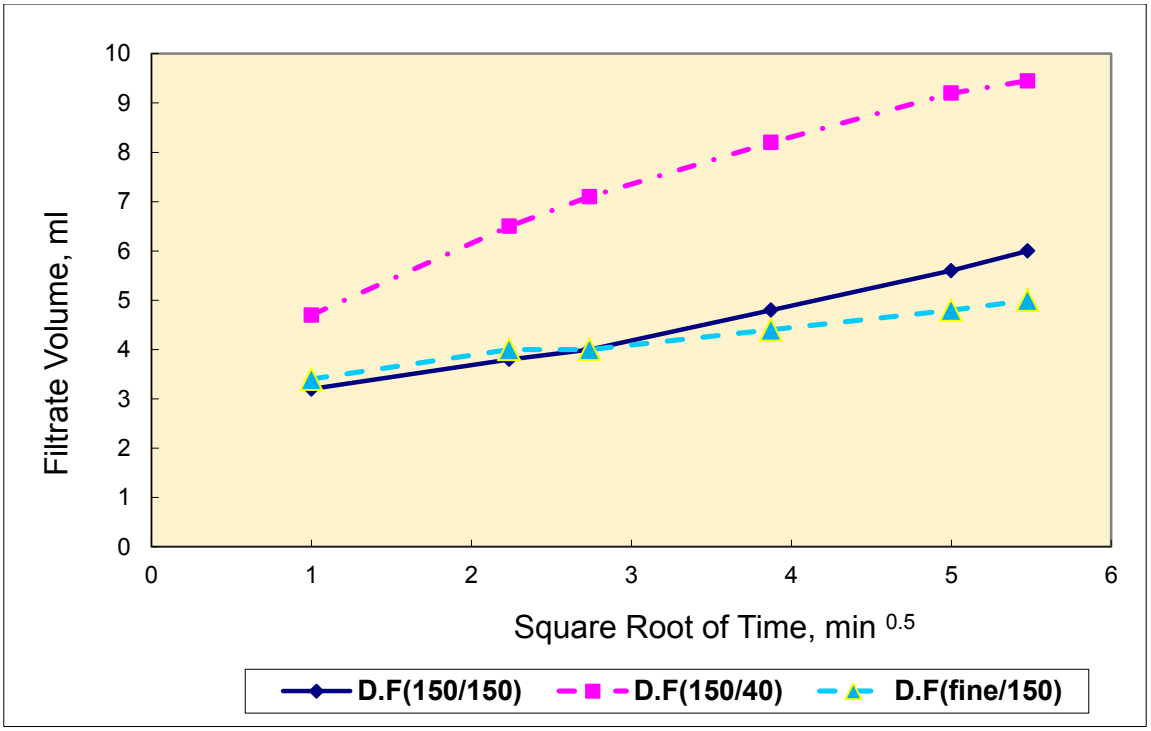

Fig. 5.16— Comparison between drilling fluids with different calcite particle size shows less damaging fluid when we have 150 micron solid acid with fine calcium carbonate particles

Fig. 5.17 shows the filter cakes which were placed at the HT/HP fluid loss and removed filter cakes after 20 hours soaking in water at 230° F and 300 psi differential pressure. **Table 5.7** gives the efficiency of filter cake removal for these three drilling fluids with different calcite particle sizes.

D.F(fine/150)	D.F(150/50)	D.F(150/150)
		
		

Fig. 5.17— Filter cakes and removed-filter cakes after 20 hours soaking in water at 230° F and 300 psi differential pressure

Table. 5.7— Efficiency of filter cake removal for drilling fluid with different calcite particle sizes

Measured Weights (gram)	**D.F(fine/150)**	**D.F(150/50)**	**D.F(150/150)**
W_{Disk}	47.55	47.60	47.68
$W_{Disk+\ ìltercake}$	58.53	62.75	68.50
$W_{Disk+\mathrm{Re}moved-\ ìltercake}$	49.75	51.61	52.31
Efficiency (%)	79.96	73.92	77.76

This set of experiments showed that the best particle size distribution for solid-acid particles to make a self-destructing filter cake, when different particles of calcium carbonate are used as weighting material in a drilling fluid, is when the solid-acid particle size is 150 microns. This size distribution shows low invasion of the drilling

mud to the formation and less damage to the formation compared to the two other particle sizes. The removing efficiency of the filter cake is also satisfying and most of the filter cake can be removed from the well at high temperature and high pressure operation conditions. The D.F (150/150) shows good filter cake removal, but as you can see from the picture the filter cake was not packed enough and could not make an impermeable filter cake.

Temperature Effect

This set of experiments was done to see the effect of temperature on filter cake removal efficiency. Temperature has an effect on the hydrolysis reaction and also on the viscosity of the drilling fluid. The experiments have been performed for drilling fluid with all the same components and the same particle sizes of calcium carbonate and solid acid, but at different temperatures. The chosen drilling fluid for all experiments in this part is **D.F (fine/150)**, which showed the best result in the previous set of experiments. The condition for all experiments was differential pressure of 300 psi and 20 hrs soaking time.

HT/HP fluid loss experiments have been done on the same drilling fluids but at temperatures of 170° F, 230° F and 320° F to find the effect of temperature on the efficiency of filter cake removal. All experiments have been done at 300 psi differential pressure to simulate the overbalance drilling situation, and 20 hrs soaking time. The filtrate was collected over a 30 minutes interval and the result of the fluid loss experiment is given in **Fig. 5.18**.

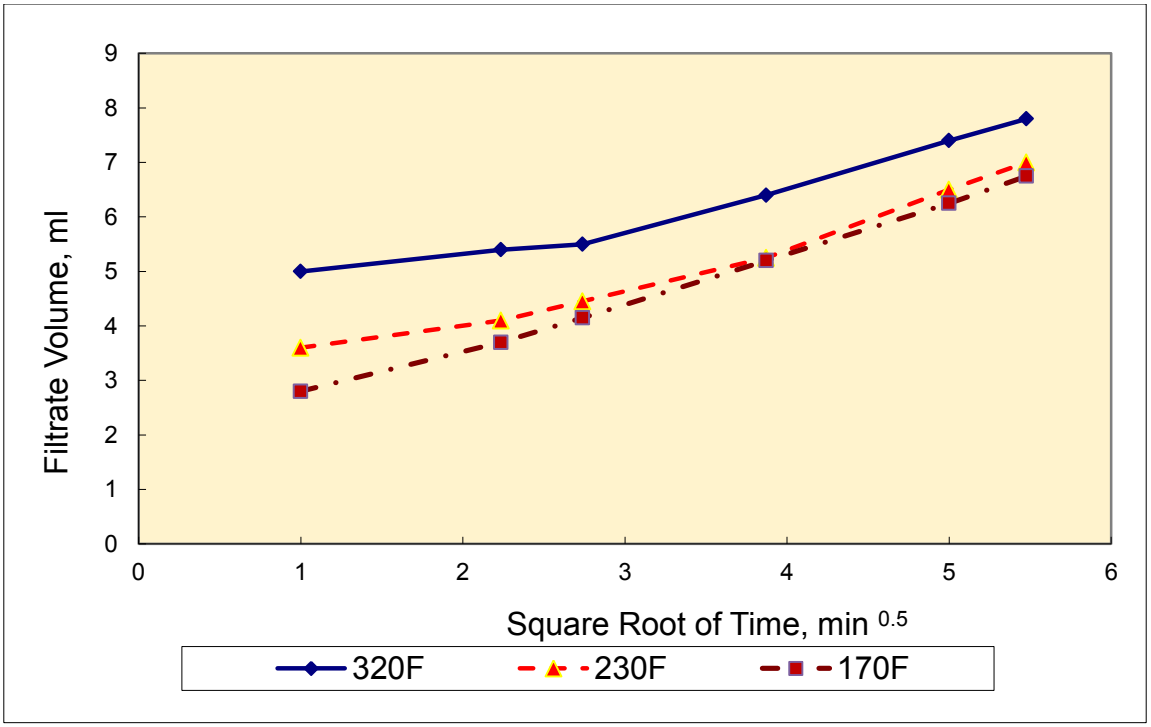

Fig. 5.18— Comparison between drilling fluid with the same composition at different temperatures, shows less damaging fluid at 170 °F

The next step is to put filter cakes in the HT/HP fluid loss again to be in contact with water at the same condition of temperature and pressure as when the filter cake was formed. The solid polylactic acids that now are part of the filter cake will start to hydrolyze at different temperatures, and after enough soaking time, they start to dissolve the calcium carbonate particles in the filter cake until finally no filter cake remains on the ceramic disk. Soaking time for all experiments was 20 hours. **Fig. 5.19** shows the filter cakes and removed filter cakes after 20 hours soaking in water at different temperatures and 300 psi differential pressure. **Table 5.8** shows the efficiency of filter cake removal for this drilling fluid at 170° F, 230° F, and 330° F.

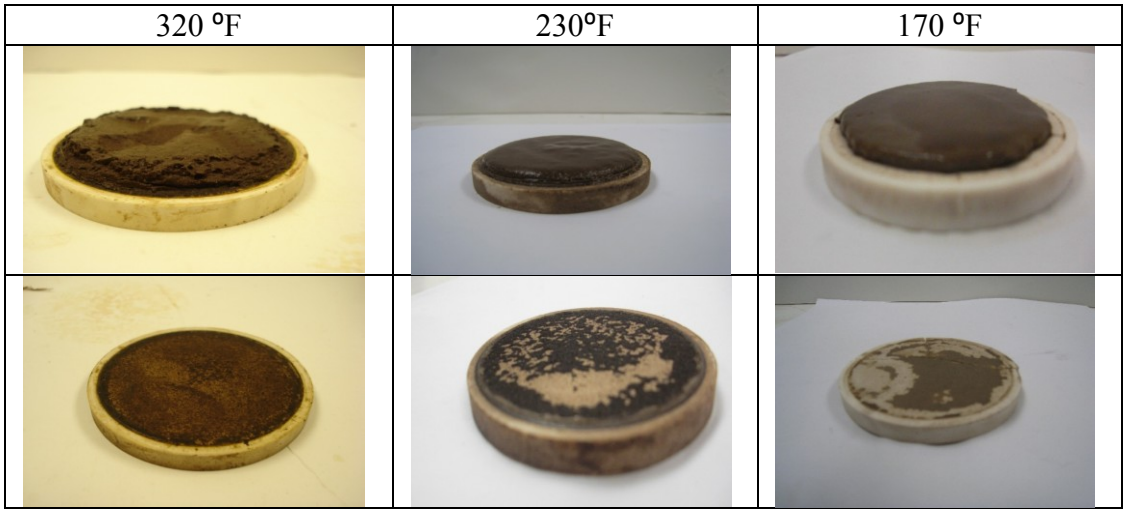

Fig. 5.19— Filter cakes and removed-filter cakes after 20 hours soaking in water at different temperatures and 300 psi differential pressure

Table. 5.8— Efficiency of filter cake removal for the same drilling fluid at different temperatures

Measured Weights (gram)	**320° F**	**230° F**	**170° F**
W_{Disk}	47.92	45.10	47.61
$W_{Disk+\ ìltercake}$	60	55	55.4
$W_{Disk+\mathrm{Re}moved-\ ìltercake}$	49.33	47.23	49.8
Efficiency (%)	88	77	72

Comparison of Return Muds at Different Temperatures

All HT/HP fluid loss experiments showed high removal efficiency of the filter cake at 170°F, 230°F, and 330°F. But the filter cake characteristics were different and also the return muds had different physical properties.

As you can see in **Fig. 5.20**, return muds are different at these temperatures. As the temperature increases, the mud becomes thicker. Effect of temperature on viscosity

could not be the only reason. As the temperature increases, the polylactic acids inside the drilling fluid want to hydrolyze and start to absorb water from the water-based mud and cause the drilling fluid to be dehydrated. In the field, dehydration may happen because of lost circulation and losing the drilling fluid into the small fractures in the formation. In our lab tests, dehydration happens between temperatures of 230° F and 260° F.

320° F	230° F	170° F
		

Fig. 5.20— Return mud comparison shows a thicker return mud at higher temperature

We have tried mutual solvents to help solve this problem, but mutual solvents did not affect the properties of the mud.

By comparison of the results of the experiments at different temperatures, we see that the mud is less damaging for 170° F (comparing the filtrate volume at HT/HP condition) and it is close to the filtrate results at 230° F. But the removal efficiency at 230° F is higher than the removal efficiency at 170° F. On the other hand, the problem of high viscosity return mud has not been seen at 230° F. Therefore 230° F is chosen to be the best temperature for running experiments and applying the self-destructing drilling fluid at HT/HP application.

Soaking Time Effect

Soaking time is the time the filter cake should be in contact with the cleaning solution. This time is needed for the solid acid particles to be hydrolyzed. As the solid acid precursor hydrolyzes, it forms an acid that attacks the carbonate or other particles. Since the solid acid precursor and calcite are intermingled during deposition, the clean up process is uniform and extensive.

This set of experiments has been done for drilling fluids with the same solid acid particle size of 150 microns and fine (around 50 microns) particle size of calcite. All experiments have been done at 300 psi differential pressure and 230^{o} F. Soaking times were 5 hrs, 13 hrs, and 20 hrs. The filter cake removal results are shown in **Fig. 5.21**. It shows that the filter cake is almost completely removed after enough soaking time. **Table 5.9** gives the efficiency of the filter cake removal for the same drilling fluid with different soaking times.

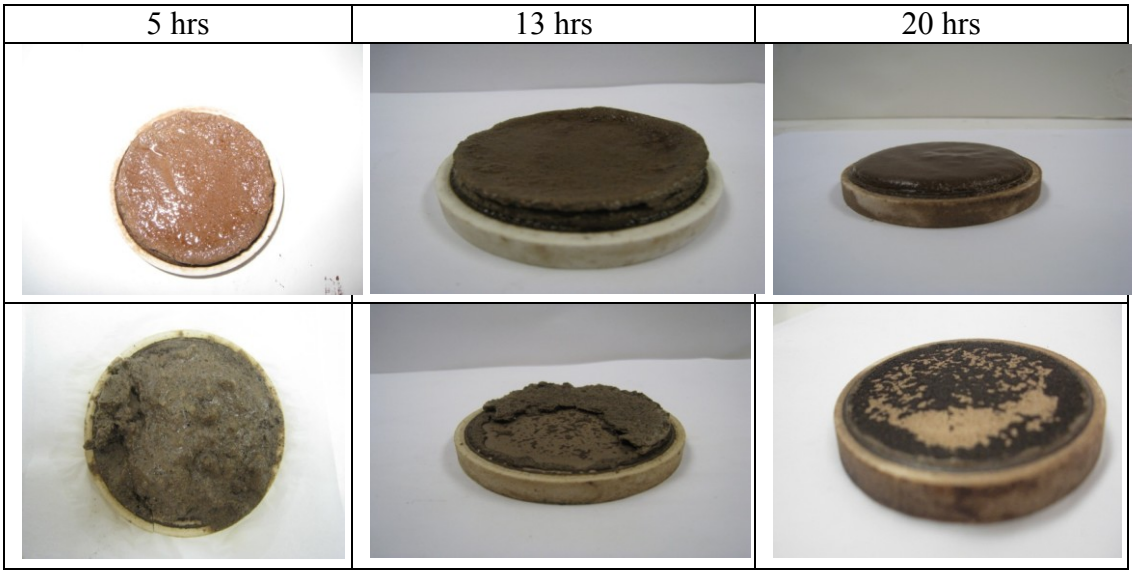

Fig. 5.21— Filter cakes and removed-filter cakes after 5 hours, 13 hours, and 20 hours soaking in water at 230° F temperatures and 300 psi differential pressure

Table. 5.9— Efficiency of filter cake removal for the same drilling fluid in different soaking times

Measured Weights (gram)	**5 hours**	**13 hrs**	**20 hrs**
W_{Disk}	48.48	46.18	47.55
$W_{Disk+\ ìltercake}$	61.88	61.85	58.53
$W_{Disk+\mathrm{Re}moved-\ ìltercake}$	61.34	52.95	49.75
Efficiency (%)	4	57	80

The results show that the self-destructing drilling fluid systems need enough time for the solid acid to be hydrolyzed and therefore remove the filter cake. Experiments showed that 5 hours is not enough soaking time and only 4% of the filter cake was

removed. 13 hours is also not a good time for soaking the filter cake in the cleaning solution. After 20 hours of the filter cake being in contact with the water (as a cleaning solution) about 80% of the filter cake was removed and a satisfying result was obtained.

Analytical Results

After the drilling fluids and filter cakes were examined with the HT/HP filter press, a chemical analysis of the returned cleaning solution was conducted. Atomic adsorption test (AA) was used to measure the concentration of calcium in the returned cleaning solution samples for different sets of experiments. The first set was the test on the drilling fluids with a variety of particle sizes of calcite and solid acid precursor as explained in parts 6.2 and 6.3. Calcium concentration of the spent soltion for drilling fluids with different particle sizes at 230° F and 300 psi differential pressure and 20 hours soaking time is given in **Table 5.10**. Also, the density was measured using a Paar densitometer model DMA-35 at room temperatures and 1 atm. The pH of the samples was measured using an ExStik EC500 pH meter.

Table. 5.10— Calcium concentration, density, and pH of the spent acid for drilling fluids with different particle sizes at 230° F, 300 psi differential pressure, and 20 hours soaking time

Drilling Fluid	Calcium Concentration, ppm	Density, g/cc	pH (24°C, 1atm)
D.F(fine/50)	1420	0.9991	5.24
D.F(fine/150)	1416	1.0021	7.36
D.F(150/50)	531	1.0012	7.85
D.F(150/150)	278	0.9992	7.93

The pH results from the table 5.10 show that the D.F (fine/50) that has the smallest particle size of the solid acid hydrolyses very quickly and produces a lot of lactic acid. This acid will dissolve calcium carbonate in the drilling fluid, but not all of the acid can be consumed. The lowest pH value and highest calcium concentration confirms that some acid produced by the hydrolysis reaction is still present in the cleaning solution.

X-Ray Diffraction (XRD) Results

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and diffracts into many specific directions. The mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

I have done XRD by using a Bruker D8 Advance Powder X-ray Diffractometer on a sample of filter cake after removal by cleaning solution, to see the elements and compounds in the sample.

Fig. 5.22 shows the results of the X-ray diffraction on the sample of removed filter cake. Results of the XRD show the presence of three materials in the sample. Calcite is the dominant compound in the sample. It shows that calcite is not dissolved by the produced acid and formed the main part of the remaining filter cake. Some traces of other materials were also detected in the sample. These materials are graphite (C) and lactose hydrate ($C_{12}H_{22}O_{11}\cdot H_2O$).

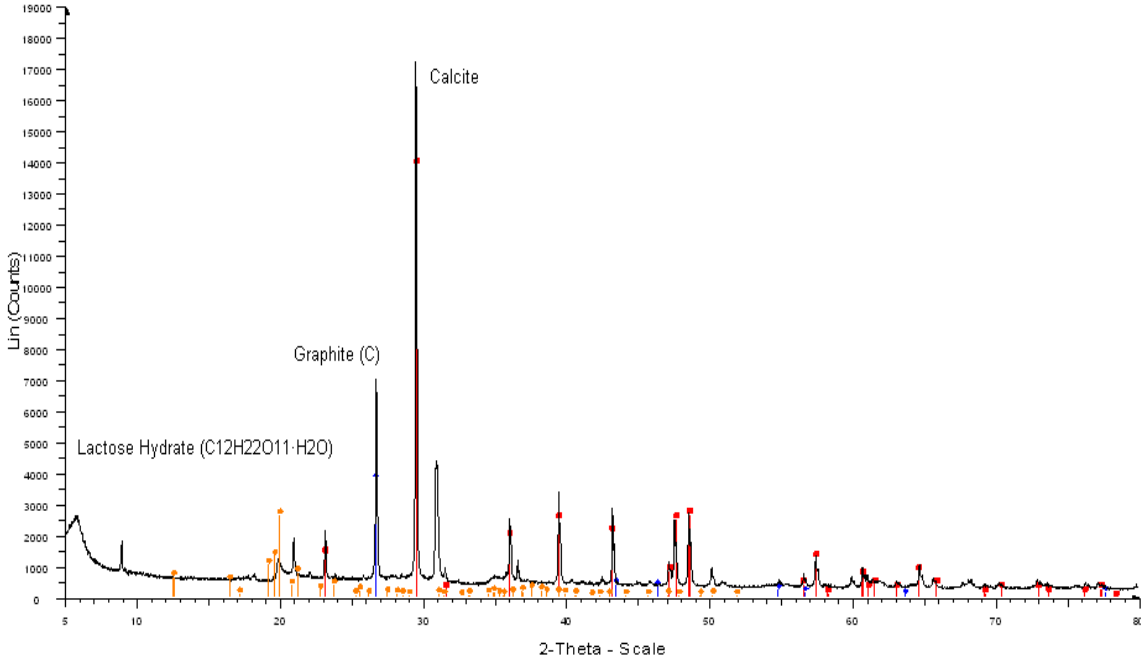

Fig. 5.22— X-ray diffraction results show presence of calcite, graphite, and some traces of lactose hydrate in the removed filter cake sample

Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography and composition. I have used an FEI Quanta 600 to see the morphology and component elements of a sample of removed filter cake. **Fig. 5.23** shows the morphology of an area of the sample of removed filter cake.

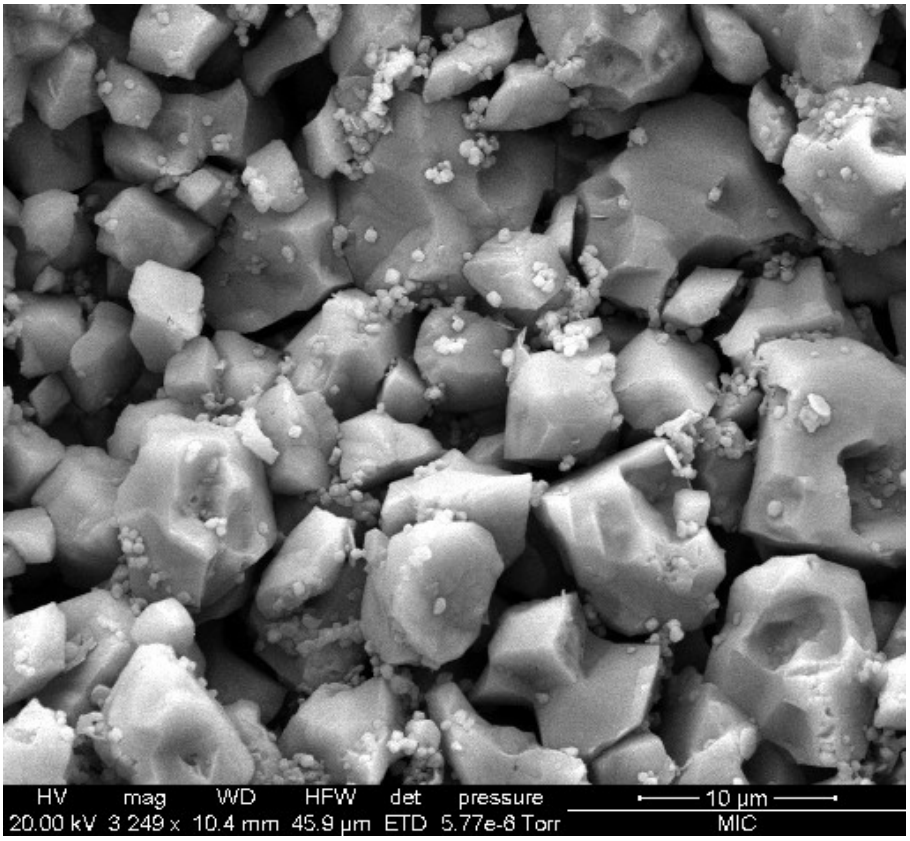

Fig. 5.23— Morphology of the surface of the sample of removed filter cake

As you can see from Figure 5.23 crystalline area of calcite has been seen in the remained filter cake sample. This result confirms presence of calcite, which has not been dissolved in generated lactic acid.

After imaging this area, dispersive x-ray spectroscopy (EDS) was performed to detect the elements that are present in this area. **Fig. 5.24** shows the EDS results. It shows presence of oxygen, silicon, calcium and carbon in this sample of removed filter cake. Trace amounts of other elements like potassium, magnesium, and iron are found in the sample detected by dispersive x-ray spectroscopy (EDS). Aluminum found in the sample is due to the aluminum sample holder and should not be considered in the results.

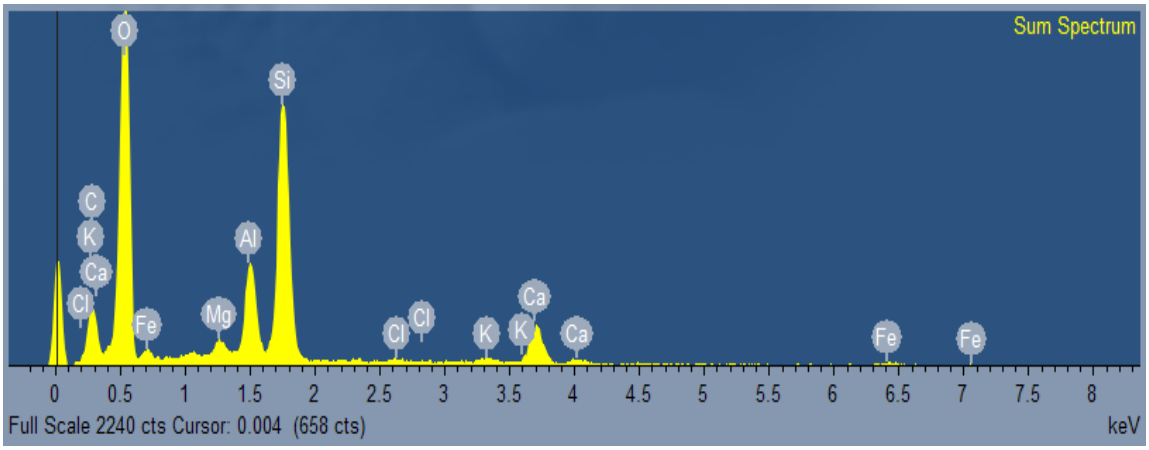

Fig. 5.24— Results of the EDS test show oxygen, silicium, calcium, and carbon in the sample of removed filter cake

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

In this study a method and composition is introduced for the drilling fluid as a self-destructing system to form filter cake in the wellbore and subterranean formations. This filter cake is formed from a formula of drilling fluid that has a mixture of solid acid precursor (solid polylactic acid) and particulate solid acid-reactive materials (calcium carbonate). Then in the presence of water, the solid acid precursor hydrolyzes and generates acid that then dissolves the solid acid-reactive material. Finally, a significant part of the filter cake has been removed by this new method. Results on this self-destructing drilling fluid are as follows:

1. A self-destructing drilling fluid has been developed based on the original gel/polymer water-based mud with the same density and rheological properties. This mud showed more than 70% filter cake removal efficiency.
2. Experiments on solid acid particle size showed that the best size-distribution of solid acid precursor and solid reactive material to make a self-destructing filter cake is fine particles of calcium carbonate used as weighting material with 150 microns polylactic acid as solid acid precursor. This particle size distribution showed low filtrate volume. It could be representative of low invasion of the drilling mud to the formation and less formation damage compared to the other particle size distributions.

3. By comparison of the results of the experiments at different temperatures, 230° F has been chosen as the best temperature for running experiments and applying the self-destructing drilling fluid at HT/HP application. The mud is less damaging at 170° F (comparing the filtrate volume at HT/HP conditions) and it is close to the filtrate results at 230°F. But the removal efficiency at 230°F is higher than the removal efficiency at 170° F. On the other hand, the problem with high viscosity return mud has not been seen at 230° F.
4. The results shows that the self-destructing drilling fluid systems need enough time for the solid acid to be hydrolyzed and therefore remove the filter cake. Experiments showed that 5 hours was not enough soaking time and only 4% of the filter cake removed. 13 hours is also not a good time for soaking the filter cake in the cleaning solution. After 20 hours of contact with the water as the only cleaning solution, about 80% of the filter cake was removed and a satisfying result was obtained.
5. Analytical results show that the drilling fluids that have the smallest particle size of the calcite can be dissolved efficiently in generated lactic acid (the highest calcium concentration in the retune cleaning solutions).
6. X-ray diffraction (XRD) results show the presence of three compounds in the removed filter cake sample. Calcite is the dominant compound in the sample. It shows that calcite is not dissolved by the produced acid, and formed the main part of the remaining filter cake. Also, some traces of

graphite (C) and lactose hydrate ($C_{12}H_{22}O_{11}\cdot H_2O$) were found in the sample of remaining filter cake.

7. Secondary electron microscopy (SEM) results show the morphology of the remained filter cake sample. It shows that the sample has crystalline area of calcite.
8. Oxygen, silicon, calcium, carbon, and traces of other elements like potassium, magnesium, and iron are found in the sample of remained filter cake, detected by dispersive x-ray spectroscopy (EDS).

Recommendations

More experiments could be done to solve problems regarding high viscosity return mud at temperatures higher than 230° F. This technology can also be tested for other mud types like oil-based mud and all-oil mud, and the results could be compared with water-based mud. This technology also can be studied from reaction kinetics point of view.

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